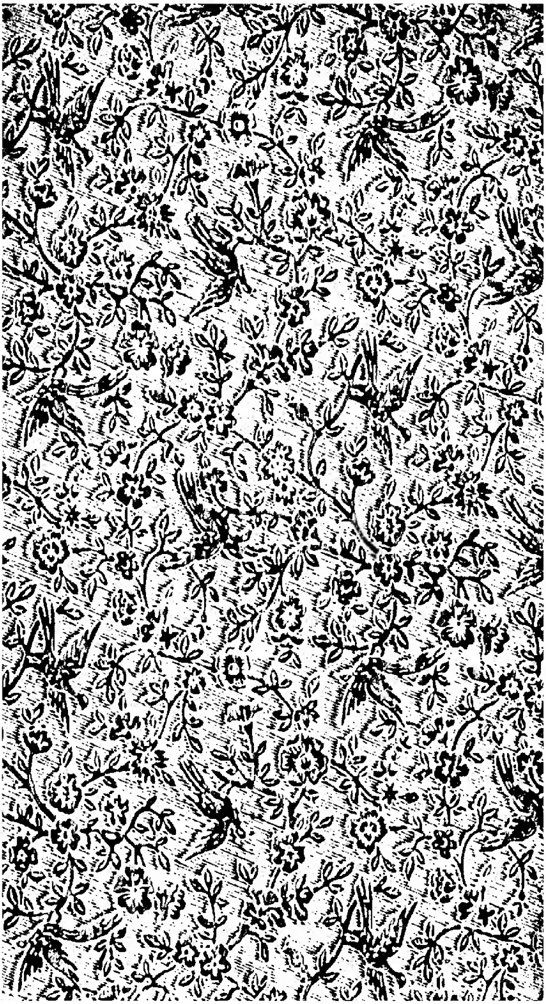

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

The Molecular Scattering of Light in *n*-Pentane. RAMA-ENKATASUBBA VENKATESWARAN (T., 1922, **121**, 2655—2663).

The Calculation of the Hydrogen Dissimilar Spectra from he Inner Movements of the Electrons. I. E. FUES (*Z. 'hysik*, 1922, **11**, 364—378).—A theoretical paper in which the neral type of the potential function in the inner field of the om has been elucidated, and methods are outlined of determining e true series constants from the course of this function. The lculation of the spectrum of an idealised cubic sodium atom gives quantum relationship of the sodium terms which is in agreement ith the new Bohr assumptions. A consistent quantitative inter-etation of the sodium spectrum will be given in the second part this paper. W. E. G.

New Spectra of Water-vapour, Air, and Hydrogen in the ctreme Ultra-violet. J. J. HOPFIELD (*Nature*, 1922, **110**, 12—733).—In an investigation of the Lyman series of hydrogen, ree new members were found. On the same spectrogram there ppeared a line λ 243·2 ± 0·2, of which the wave-length agrees ithin limits of experimental error with the equivalent wave-ngth (λ 248) for the *L* critical potential of oxygen. The con-tions of the observation of this line indicate the transparency of

hydrogen in this region, and the termination on the long wave-length side of λ 243 of the great absorption band of hydrogen which begins at about λ 850. Water-vapour gives a spectrum in the ultra-violet extending to about λ 900, and consisting of oxygen lines, hydrogen series lines, the secondary spectrum of hydrogen, and some bands probably not due to hydrogen. For air, a spectrum was obtained to λ 350. A. A. E.

Effect of Pressure on the Band Spectra of Nitrogen. JEAN HUDDLESTON (*Physical Rev.*, 1921, **18**, 327).—An investigation of the negative pole bands and the second group of positive bands produced by nitrogen or air at pressures ranging from one to six atmospheres by means of a spark discharge, using a transformer or small induction coil. In nitrogen at one atmosphere pressure, the positive and negative bands were of about the same strength, whilst as the pressure increased there was gradual formation of a continuous spectrum, the positive and negative bands being similarly affected. With air, the negative bands were stronger than the positive. In the region of the first group of positive bands, which was observed visually, there was no evidence of any band structure at or above one atmosphere pressure. A. A. E.

Determination of the Wave-lengths of 118 Titanium Lines by means of the Interferometer. FREDERICK L. BROWN (*Astrophys. J.*, 1922, **56**, 53—70).—By the use of a Fabry-Perot interferometer and a Hilger spectrograph of the constant-deviation prism type, a number of titanium lines between λ 4263·134 and λ 6261·097 have been measured in comparison with the cadmium line λ 6438·4696. A. A. E.

The Ultra-violet Absorption Spectra of Pyridine and *iso*Quinoline. H. FISCHER and P. STEINER (*Compt. rend.*, 1922, **175**, 882—884; cf. Henri and Steiner, A., 1922, i, 928).—A quantitative study of the absorption spectra of pyridine and *iso*quinoline in hexane solution has given new results. In the case of pyridine, the bands which correspond with those of benzene are replaced by a single band, whilst five new bands were observed in the region of greater wave-length. The curve obtained for *iso*quinoline resembles that given by naphthalene, but is situated as a whole towards the region of shorter wave-length. Certain general similarities are also found between the spectra of pyridine and *iso*quinoline. H. J. E.

Luminescence of Zinc Oxide above Red Heat. E. L. NICHOLS (*Physical Rev.*, 1921, **17**, 429—430).—Zinc oxide, whilst not photoluminescent or responsive to *X*-rays, is susceptible to excitation by the hydrogen flame (cf. Nichols and Wilber, A., 1922, ii, 105, 806) with the development of (*a*) a red band which appears when the oxide is heated at 568°; at 700° it is displaced by a yellowish-green band, (*b*) a yellowish-green band which disappears at about 940°. The point of maximum brightness, somewhat above 800°, may indicate the occurrence of some molecular transformation.

A. A. E.

Chemi-luminescence and the Thermochemical Behaviour of Organo-magnesium Compounds. I. LIFSCHITZ and OTTO E. KALBERER (*Z. physikal. Chem.*, 1922, **102**, 393—415).—An investigation on the mechanism of the luminescence brought about by chemical reactions. It is shown that ethereal solutions of magnesium phenyl, *p*-bromophenyl, *o*-tolyl, *p*-tolyl, *p*-diphenyl, and α-naphthyl bromides in the presence of air all give rise to a white luminescence, whilst in the presence of oxygen a blue luminescence varying in shade is observed. On the other hand, magnesium ethyl, benzyl, *n*-propyl, and camphor bromides, magnesium ethyl, *n*-propyl, and *iso*amyl iodides, magnesium *n*-propyl and triphenylmethyl chlorides, and all compounds in which the magnesium is directly linked with an aliphatic carbon atom, do not give rise to luminescence under the influence of air or oxygen in ethereal solution. The luminescence gains in intensity in the above-named compounds with increasing molecular weight, and the light gives a continuous spectrum which extends from the green to the blue, and in no case does it correspond with the absorption spectrum of the ethereal solution. The dry magnesium halogen derivatives, irrespective of whether they are aliphatic or aromatic, give a much more intense light when in contact with air or oxygen than the ethereal solutions; here the light is of a green colour and gives a continuous spectrum. Among other reactions which are accompanied by luminescence, the authors note the action of nitrous oxide and ethyl nitrite, nitric oxide and ethyl nitrate, nitrogen dioxide and acetyl chloride, carbon dioxide and water, carbon monoxide and benzene triozonide in benzene solution, and chloropicrin and magnesium phenyl bromide. It is shown that a high velocity of reaction is not a necessary cause of luminescence; large heat changes or active masses are also not at all determinative of luminescence. The heat of formation of a number of additive compounds of ethyl ether and Grignard compounds and the heat of reaction of these substances with water have been determined calorimetrically. In the case of the Grignard compounds, the authors are of the opinion that either the Grignard compound (I) or the mono-ether derivative (II) is the seat of the luminescence, $R\cdot Mg\cdot X$ (I) $+ n$ mols. ether $\rightleftharpoons R\cdot Mg\cdot X$, ether (II) $+ n$ mols. ether $\rightleftharpoons R\cdot Mg\cdot X, 2$ ether.

J. F. S.

Theory of Radiation Transformation. I. General Mechanism of Photochemical Processes. FRITZ WEIGERT (*Z. physikal. Chem.*, 1922, **102**, 416—437).—A theoretical paper in which the mechanism of the absorption of light and its conversion, when absorbed, into such a form that it can bring about a chemical reaction is discussed. J. F. S.

The Photochemistry of Hydrogen-Chlorine Mixtures. FRITZ WEIGERT (*Z. Elektrochem.*, 1922, **28**, 456—458).—A study of the Draper effect, and the changes in density which occur on illumination of mixtures of chlorine and hydrogen with light of short wave-length. On exposure of the gaseous mixture to light from an electric spark, a wave of cloud spread out from the illumi-

nated region which synchronised with a movement of the surface of a water manometer in contact with the gas. The initial stages in the propagation of the wave and its mode of formation were examined by a photographic method. No appreciable change was observable until 1/160 second after illumination, when bright regions appeared in the tube near the point of entrance of the light. This brightness reached a maximum in 1/40 second, and had entirely disappeared in 1/10 second. The rate of combination between hydrogen and chlorine thus appears to reach a maximum 1/40 of a second after illumination. The chain-like mechanism postulated by Bodenstein and Nernst for this reaction provides the most convenient interpretation of this time interval. If 10^6 molecules be converted one after the other by one energy quantum, it can be shown that each element in the chain takes 10^{-8} seconds to be completed. This interval of time occurs frequently in the modern atomic theory of chemical action. W. E. G.

Effect of *X*-Rays on Chemical Reactions. O. R. OLSON (*Science*, 1922, **56**, 231).—Exposure to *X*-rays of *cyclo*hexanol contained in a brass cell, resulted in the dissolution to a greenish-blue solution of about 0·1 g. of copper. Calculations based on the conditions of the experiment indicate that the *X*-rays produced some kind of trigger action. Mesitylene showed a similar behaviour. On account of the large effect produced by relatively small amounts of energy, the possible preparation of organic compounds by the use of *X*-rays is indicated. A. A. E.

Adsorption of Radium-*B* and Radium-*C* by Ferric Hydroxide. JOHN ARNOLD CRANSTON and ROBERT HUTTON (T., 1922, **121**, 2843—2849).

The Ionisation Potential of Selenium Vapour. A. D. UDDEN (*Physical Rev.*, 1921, **18**, 385—388).—The ionisation potential of selenium vapour is found to be 12·7 ± 0·4 volts. If this potential is substituted for V in the equation $\nu = Ve/h$, the limiting frequency of the spectrum of selenium vapour is about 980 Å. A. A. E.

The Ionisation of Abnormal Helium Atoms by Low Voltage Electronic Bombardment. FRANK HORTON and ANN CATHERINE DAVIES (*Phil. Mag.*, 1922, [vi], **44**, 1140—1146).—The formation and maintenance of an arc in helium with alternating *E.M.F.* at about 5 volts has been described by Kannenstine (*Astrophys. J.*, 1922, **55**, 345). This occurs only if the helium contains abnormal helium atoms activated by voltages above 20·4. This result indicates the possibility of ionising abnormal helium atoms by electrons having 4·8 volts energy. In the present paper, abnormal atoms are produced by the action of radiation from an auxiliary side-tube of the apparatus, and the effect of bombarding these with a stream of electrons is investigated. Ionisation commenced at about 4·5 volts. Below this voltage the ionisation was very slight. Thus no abnormal atoms could have been present which had absorbed radiation corresponding with voltages greater

than 21·2 volts. The abnormal atoms responsible for the maintenance of low-voltage arcs must correspond therefore with 20·4 and 21·2 volts. There is no necessity to assume the existence of metastable helium atoms. W. E. G.

The Temperature Ionisation of Elements of the Higher Groups in the Periodic Classification. MEGH NAD SAHA (*Phil. Mag.*, 1922, [vi], **44**, 1128—1139).—The degree of ionisation of the alkaline-earth metals, as measured by the intensity of the spectrum lines in the sun, is greater than that of the alkali metals with similar ionisation potentials. This is due to differences in the rates of loss of the outer electrons under the influence of external forces, and in the speeds of recombination of the displaced electron with the positively charged atoms. The two outer electrons in bivalent elements will be displaced with equal ease by bombarding electrons, and, for elements with the same ionisation potentials, the number of successful hits by the collision of an electron with a bivalent atom will be twice as great as with a univalent atom. A steric factor also operates in the same direction. Owing to the protective action of the remaining electron, the recombination of the displaced electron with the positively charged bivalent atom will be slower than in the case of a univalent atom. The equation deduced by Boltzmann for the steric factor in the formation of diatomic gases is applied to the case of the combination between an ionised atom and an electron, and it is shown that the effective ionisation potential $I_e = I - 2{\cdot}3RT \log (n_a n_b)/23{,}000$ volts. The variation in the effective ionisation potential of the elements with temperature is calculated from this equation, and the results are in agreement with the intensities of the lines in the stellar spectra for uni-, bi-, ter-, quadri-, and quinque-valent elements. The successive stages in the ionisation of a multivalent element are shown to follow in quick succession as the temperature rises.

W. E. G.

Inelastic Collisions of Electrons in Vapours of certain Compound Molecules. PAUL D. FOOTE and F. L. MOHLER (*Physical Rev.*, 1921, **17**, 394).—The ionisation potential of zinc ethyl is 12 volts and the resonance potential about 7 volts. The ionisation potentials of zinc chloride and mercuric chloride are 12·9 volts and 12·1 volts, respectively. In the case of carbon monoxide, there are two ionisation potentials, namely, 10·1 and 14·3 volts. Besides these inelastic collisions, electrons undergo the following velocity losses without producing ionisation: 6·4, 12·1, 13·6, 19·1, 21·9, and 24·6 volts. There is a marked contrast in the behaviour of sodium and potassium chlorides on the one hand and calcium on the other; vapours of the former are highly ionised at 2 mm. pressure, preventing measurements of the ionisation potential, whilst calcium vapour is not appreciably ionised at 700°.

A. A. E.

Solubility of Barium Selenate. JULIUS MEYER and WALTER FRIEDRICH (*Z. physikal. Chem.*, 1922, **102**, 369—387; cf. A., 1922, ii, 70).—The equivalent conductivity of sodium and potassium

selenate has been determined at 0°, 5°, 18°, 25°, 35°, and 50° for concentrations between $v=2$ and $v=2048$. From the conductivity values the mobility of the selenate-ion has been calculated for various concentrations for 18° and 25°. Among the data obtained, the following values of the ionic conductivity of the selenate-ion at infinite dilution are quoted, $\lambda^{18°}=64·01$ and $\lambda^{25°}=73·68$ from sodium selenate and $\lambda^{18°}=65·12$ and $\lambda^{25}=74·80$ from measurements with potassium selenate, the mean values accepted being 64·57 and 74·24, respectively. The temperature coefficient of the ionic conductivity of the selenate-ion at infinite dilution is obtained from the formula $x_{t_1}=x_{t_2}[1+c(t_1-t_2)+c'(t_1-t_2)^2]$, in which $c=210\times10^{-4}$ and $c'=49\times10^{-6}$. The transport numbers of the anions of sodium, potassium, and barium selenate have been calculated. In every case the value decreases with increasing concentration. From the conductivity measurements, the solubility of barium selenate at 25° is calculated to 82·5 mg. per litre of water, whilst the direct determination of this quantity gives the values 79·2 and 82·0 mg. per litre. J. F. S.

Conductivity of Aqueous Solutions of Iodic Acid and the Limiting Value of the Equivalent Conductivity of the Hydrogen-ion. CHARLES A. KRAUS and HENRY C. PARKER (*J. Amer. Chem. Soc.*, 1922, **44**, 2429—2449).—The apparatus employed and the precautions observed in carrying out conductivity measurements with iodic acid at concentrations down to $5\times10^{-5}N$ are described. The measurements were carried out in glass and quartz cells to determine the influence of impurities on the conductivity of acid solutions at low concentrations. It was found that the conductivity curve exhibits a maximum due to impurities with water having a specific conductivity above $0·1—0·2\times10^{-6}$. The influence of alkali derived from the glass is, if anything, greater than that of the impurities present in the water having a specific conductivity of $0·8\times10^{-6}$. Conductivity measurements with iodic acid in quartz cells with water having a specific conductivity $0·1\times10^{-6}$ were carried to concentrations as low as $0·5\times10^{-6}$ with a relative precision of a few hundredths per cent. Extrapolating on the assumption that the law of mass action is followed as a limiting law at low concentrations, the value 389·55 is found for Λ_∞ at 25°, which may be accepted as a lower limit to the possible value of this constant. The mass-action constant corresponding with the extrapolation has a value 0·0717. Iodic acid is thus a much stronger electrolyte than potassium chloride. The conductivity of the iodate-ion has been deduced for 25° on the assumption that the Λ_∞ value between 18° and 25° changes in the same proportion as the conductivity of a 0·0015N-solution of the acid. The value 39·62 was thus found for the conductivity of the iodate-ion. For the conductivity of the hydrogen-ion at 25°, the value 349·93 is obtained. Assuming that the limiting value of the equivalent conductivity of iodic acid between 18° and 25° varies in the same way as that of a 0·001N-solution of the same acid, 349·62 is found for the value of Λ_∞ of iodic acid at 18°. Assuming the value

34·0 for the equivalent conductivity of the iodate-ion at 18°, there is obtained the value 315·62 for the conductivity of the hydrogen-ion at 18°. J. F. S.

Conductivity of Solutions of Salts in Phenol. CHARLES A. KRAUS and HERMAN F. KURTZ (*J. Amer. Chem. Soc.*, 1922, **44**, 2463—2468).—The electrical conductivity of solutions of tetramethylammonium iodide in phenol has been determined at 50° for concentrations from $0·07N$ to $1\times10^{-4}N$. The conductivity curve is accounted for by Kraus and Bray's equation $(c\gamma)^2/c(1-\gamma)=D(c\gamma)^m+K$, in which $D=0·70$, $m=1·28$, and $K=2·25\times10^{-4}$. The equivalent conductivity at infinite dilution is 16·67. The conductivity of sodium iodide solutions in phenol has been measured at the same temperature for concentrations between $1\times10^{-4}N$ and $1·6\times10^{-3}N$. It is shown that sodium iodide is much less ionised than tetramethylammonium iodide in phenol solution. Solutions of tetramethylammonium iodide in phenol are not appreciably hydrolysed. J. F. S.

Calibration of Cells for Conductivity Measurements. CHARLES A. KRAUS and HENRY C. PARKER (*J. Amer. Chem. Soc.*, 1922, **44**, 2422—2428).—The necessary data for making up standard potassium chloride solutions according to the weight method for calibrating conductivity cells are correctly given by Kohlrausch and Holborn for $1·0N$-solutions only; their directions for making up standard solutions of concentrations 0·1, 0·02, and $0·01N$ are in error. In the case of the $0·1N$-solution, the error is 0·10% and for the $0·01N$-solution 0·54%. The conductivity data as given by Kohlrausch and Holborn are not sufficiently precise for present-day purposes, and it is suggested that the values obtained by Kohlrausch and Maltby (A., 1900, ii, 61) be employed. The necessary data are given in the present paper for making up 1·0, 0·1, and $0·01N$-solutions of potassium chloride by the weight method. The specific conductivity of $0·1N$ (at 18°) potassium chloride has been determined at 25° in terms of its value at 18°. Assuming for the specific conductivity at 18°, the value 0·011203, as determined by Kohlrausch and Maltby, the specific conductivity at 25° is found to be 0·0128988. This value may serve for the purpose of calibrating cells at 25°, thus avoiding the necessity of making determinations at 18°. J. F. S.

Free Energy of Dilution of Alcoholic Solutions of Lithium Chloride and the Effect of the Solvent on the Activity of the Ions. J. M. PEARCE and H. B. HART (*J. Amer. Chem. Soc.*, 1922, **44**, 2411—2419).—The *E.M.F.* of concentration cells, both with and without ion transport, containing alcoholic solutions of lithium chloride have been measured at 25°, 30°, and 35°. From the data thus obtained the authors have calculated the transport number of the lithium-ion in ethyl and methyl alcohols at various dilutions and find a value of about the same size as that for aqueous solutions. The transport number increases with dilution and with increase in temperature. The decrease in free energy and in the

heat content accompanying the dilution has been calculated. The *E.M.F.* of cells containing two solvents in which an alcohol solution of various concentrations is opposed to an $0{\cdot}1N$-solution of lithium chloride in water have also been measured at the same temperatures. The decrease in free energy and in heat content accompanying the transport of 1 gram-molecule of lithium chloride from its solution in alcohol to an $0{\cdot}1N$-solution in water has been calculated. Using the values of free energy decrease obtained for these cells, the free energy of dilution of lithium chloride in ethyl and methyl alcohols from any concentration to a concentration of 1 gram-molecule in 10,000 gram-molecules of solvent has been calculated. The apparent geometric mean activities of the ions of lithium chloride have been calculated for a series of concentrations expressed in gram-molecules per 100 gram-molecules of solvent. J. F. S.

The Electromotive Behaviour of Silver–Cadmium Alloys. Erling Schreiner, Ivar Bull Simonsen, and Ole H. Krag (*Z. anorg. Chem.*, 1922, **125**, 173—184).—The *E.M.F.* of the cell Ag–Cd alloy|NCdSO$_4$(Ag)|Cd was determined. As the amount of cadmium was increased to 30%, the potential gradually decreased, indicating a solid solution of the metals. A sudden change of potential occurs when the amount of cadmium reaches 60 atom. %, indicating the formation of the compound Ag_2Cd_3; similarly, another sudden change occurs at 80 atom. % of cadmium, indicating the compound $AgCd_4$. Between 93 and 100 atom. % of cadmium, the results are again in harmony with the assumption of a solid solution. Very few measurements were carried out for alloys with 75—80 atom. % of cadmium, and therefore the formation of the compound $AgCd_3$ was not detected. On keeping the alloy for some time (three to four months), a new compound, AgCd, is indicated. The temperature coefficient of the *E.M.F.* of the alloys was also determined, and was found to vary with the composition of the alloy. The authors point out the difficulty of getting trustworthy results on account of changes at the surface of the electrode, and also show that the heat of formation of the alloy cannot be calculated from the electrical measurements. W. T.

The Hydrogen Electrode under High Pressures. W. R. Hainsworth (*Science*, 1921, **53**, 578).—From a study of the variation of the *E.M.F.* of the cell H_2|HCl($0{\cdot}1N$-HCl),HgCl|Hg with pressure, it is concluded (*a*) that the "thermodynamic environment" is not appreciably changed by the molecular hydrogen in solution, or by compression, and (*b*) that the fugacity (or effective pressure) of hydrogen can be calculated up to 400 atmospheres from the equation of state developed by Keyes. A. A. E.

The Behaviour of Metals on Cathodic Polarisation. G. Tammann and W. Wiederholt (*Z. anorg. Chem.*, 1922, **125**, 67—85).—The authors have investigated the recovery after short circuiting of a cell composed of two metals immersed in a solution of a salt of the less noble metal. If the *E.M.F.* is plotted against the logarithm of the time, three straight lines are obtained; these

three curves being represented by expressions of the following form: $E=E_1+(E_1 \log . t)/\log a_1$. The value of the constant for two of the curves depends on the external conditions; the constant for the third curve depends only on the nature of the electrode and the polarising ion. Partial covering of the surface of the more noble metal by the less noble increases the potential almost to the value for the less noble. W. T.

Theory of Electrolytic Ions. Simple Method of Determining the Limiting Molecular Conductivity of Strong Electrolytes. RICHARD LORENZ and A. LANDÉ (*Z. anorg. Chem.*, 1922, **125**, 59—66).—The authors assume that strong electrolytes are completely ionised, and that the increase in conductivity on dilution is due to an increase in the mobility of the ions. Thus, instead of the expression $\mu=\alpha(u_0+v_0)$, the expressions $\mu=(u+v)$ and for the limiting value $\mu_0=(u_0+v_0)$ are obtained. The rate of increase of the mobility with dilution, *i.e.*, $u/u_0=x$ and $v/v_0=y$, is characteristic for each ion. The authors have, however, found that, for example, $1-x_K/1-y_{Cl}$=constant$=a$, similarly $1-x_{Na}/1-y_{Cl}$=constant$=b$, and $1-x_{Na}/1-x_K$=constant$=c$. These values are given as $a=1{\cdot}079$, $b=1{\cdot}396$, and $c=1{\cdot}292$. These values are easily determined for such salts as potassium chloride and sodium chloride, which are therefore defined as normal electrolytes; hence, to find the limiting conductivity of an acid, the sodium or potassium salt is prepared, and in the case of a base, the chloride. Thus in the case of the anion A^-, the conductivity of the potassium salt is determined in at least two concentrations, *e.g.*, at $C_1\mu_1=K^+{}_1+v_1$ and at $C_2\mu_2=K^+{}_2+v_2$ (K^+=ionic mobility of the potassium ion). If $y=v/v_0$; then from the above $1-x_1/1-y_1=1-x_2/1-y_2$=constant; hence v_0, *i.e.*, the limiting conductivity of the anion, can be determined. W. T.

Free and Total Energy Changes in the Reduction of Quinones. JAMES B. CONANT and LOUIS F. FIESER (*J. Amer. Chem. Soc.*, 1922, **44**, 2480—2493; cf. A., 1922, ii, 547).—A continuation of previous work. The temperature coefficients of the oxidation–reduction potentials of a number of derivatives of *o*-benzoquinone, naphthaquinone, and anthraquinone have been measured by two methods. The free energy, total energy, and latent heat of reduction in aqueous solution have been calculated from the potentials and the temperature coefficients. The free and total energy are shown to vary greatly with the different types of quinones measured. The total energy change, in aqueous solution, agrees with the total heat change for the solids as measured calorimetrically, since the heats of solution are small. A method is developed for measuring the free energy of reduction of quinones in alcoholic solutions. By means of this method, a number of substances have been investigated which are too insoluble to measure in aqueous solution. The oxidation–reduction potential of a given quinone is slightly greater in alcoholic than in aqueous solution. It is practically identical in 50, 75, and 95% alcoholic

solutions. Preliminary measurements indicate that the temperature coefficient is greater than in aqueous solution. An equation has been developed which relates the free energy change referred to the solids to the potential in a given solution and the solubilities of the quinone and quinol. The differences in the oxidation potential as measured in two different solvents can thus be calculated from solubilities. The discrepancy between the present value for *p*-benzoquinone and the value obtained by Haber and Russ (A., 1904, ii, 309), is shown to be due to an assumption made by these authors which is invalid. J. F. S.

The Specific Resistance and its Temperature Coefficient and the Thermo-electromotive Force of Ternary Mixed Crystals. KURT FISCHBECK (*Z. anorg. Chem.*, 1922, **125**, 1—27).—The specific resistances and their temperature coefficients of ternary alloys of gold, silver, and copper were measured. The thermo-electromotive force of the alloys against copper were also determined, the ends of the wires being kept at 100° and 0°. The paper also contains a *résumé* of the literature on the specific resistance, its temperature coefficient, and the thermo-electromotive force of ternary mixed crystals. W. T.

Effect of Absorbed Hydrogen on the Thermo-electric Properties of Palladium. R. M. HOLMES (*Science*, 1922, **56**, 201—202).—Strip palladium which had been heated at 700° in a vacuum and cooled in hydrogen was found to possess a thermo-electric power of 73% of that of the gas-free metal, whilst saturation of the strip by electrolysis resulted in a reduction to as little as 28%. The effect of absorbed hydrogen is to increase the effective electron density in palladium, since $e=K \log (n_a/n_b)$, where e is the thermo-electric power of a couple, K is a constant, n_a and n_b are the effective electron densities in the two materials forming the circuit. A. A. E.

Specific Heats. III. Specific Heats of Isomerides and of Aromatic Hydrocarbons in the Solid State. M. PADOA (*Gazzetta*, 1922, **52**, ii, 202—207; cf. A., 1921, ii, 15; 1922, ii, 348). —Measurements have been made of the specific heats of dihydroxybenzenes, succinic, maleic, and fumaric acids, methyl oxalate, trihydroxybenzenes, and various hexose sugars. The results show that the specific heats of solid isomeric compounds often differ and are sometimes less for those containing the more energy. The values for maleic and fumaric acids at various temperatures indicate inversion of the stability relations of the acids as the temperature rises. The specific heats of optical antipodes are identical. For polynuclear benzenoid hydrocarbons the mean atomic heat varies, the differences depending on the different arrangement of the linkings in the molecules and in the crystals. The mean atomic heat has the same value in the isomeric compounds, anthracene and phenanthrene, the numbers, directions, and energies of the linkings being the same in the two cases. T. H. P.

A Modification of van der Waals's Equation. W. P. BOYNTON and ARTHUR BRAMLEY (*Physical Rev.*, 1922, 20, 46—50).—The equation $(p+a/v^2)(v-b)=RT(1+\psi^2/T^2)$, where ψ is a characteristic temperature, is proposed as a modification of that of van der Waals; it is claimed to represent more closely the behaviour of carbon dioxide and other substances, and to give better values for the ratio T_c/p_cv_c. It is shown that not only the energy but also the specific heat and entropy derived from this equation approach zero values at the absolute zero, in agreement with conclusions drawn from Nernst's investigations. Theoretical formulæ for specific heat (c_v), internal energy, and entropy as functions of T and v are derived. A. A. E.

A New Formula for the Internal Pressure of Liquids. Criterion of Molecular Association in a Liquid. N. VASILESCU KARPEN (*Bull. Acad. Sci. Roumaine*, 1922, 8, 22—26).—The internal pressure K of a liquid can be calculated from the formula $K=T\alpha/\mu-p$, where α is the coefficient of expansion and μ the coefficient of compression of the liquid. The following values of K have been calculated: ethyl ether, at 168°, 1900; ethyl alcohol, at 90°, 3300; water, at 200°, 10,300; ethyl chloride, at 8°, 2700; methyl alcohol, at 20°, 3900. In each case, the ratio K/p_c, where p_c is the critical pressure, is approximately equal to 50. The values of K found by van der Waals for these liquids were about 25% lower except in the case of water, for which the value found was 10,700. For most liquids, it is found that at lower temperatures the value of K/p_c is higher than normal, indicating association. If dq is the heat absorbed by dissociation of the molecules and K is the internal pressure of the non-associated liquid, the above equation can be modified into the form $J.dq/dv=T.\alpha/\mu-K-p$. The heat dq is generally positive, but in the case of water is negative. It is concluded that water is associated at all temperatures below 200° and that dissociation of the complexes is exothermic.
E. H. R.

The Determination of Temperatures of Combustion of Gases. F. POLITZER (*Z. angew. Chem.*, 1922, 35, 683—684).—The theoretical maximum temperature attainable by the combustion of any gas or mixture of gases can be calculated graphically as follows. The increase in energy content in calories of 1 gram-molecule of the different gases considered, at constant pressure above the energy content at 0°, is plotted against the temperature in degrees C. Thus the molecular heat at constant pressure $Cp=U/dT$. Such curves are identical for gases of the same molecular complexity. Considering, for example, the combustion of carbon monoxide with its exact equivalent of oxygen to carbon dioxide, the heat of reaction is 68,000 cal. The point where the carbon dioxide curve cuts this abscissa gives the theoretical maximum temperature of the reaction (under adiabatic conditions) reading from the x-axis, of 4850°. Cases in which there is an excess of one reagent, or indifferent gases are present, can be dealt with by curves in which the energy contents of the different components

of the burnt mixture are added together. Such curves will, of course, be steeper indicating lower flame temperatures. A correction is necessary for the dissociation of carbon dioxide and water vapour which takes place to a marked extent at temperatures above 2000°. At 4850°, the dissociation of carbon dioxide is no less than 99%. The proportion of dissociated gaseous product must be considered as if it were an addition of an indifferent gas. If x is the degree of dissociation of carbon dioxide and y that of water vapour, and if m molecules of water vapour are present to 1 mol. of carbon dioxide, then the number of molecules of diatomic gases present in the burnt mixture to each molecule of carbon dioxide or water vapour is $1{\cdot}5(x+my)+a/1+m-(x+my)$, a being the dilution with indifferent gas. Corrected values for flame temperatures can be obtained from equations thus developed by methods of trial and error. Figures so obtained for the combustion of different gases with their equivalents of air are: hydrogen 2130°, carbon monoxide 2095°, acetylene 2200°, illuminating gas 1975°. The latter compares with Berkenbusch's experimental result of 1800° with a bunsen burner. C. I.

Application of the Nernst Heat Theorem to Dilute Solutions. KARL F. HERZFELD (*Z. Elektrochem.*, 1922, **28**, 460—463).—An attempt to calculate the bound energy, G, of molar solutions from the normal potentials, and the solubility of sparingly soluble salts. The value $1/\gamma(G_X-G_{Ag})$ is derived for a number of ions, where G_X is the bound energy of the ion X. The greater the heat of hydration of this ion, the greater is the value of G_X. From these values, the solubilities of a number of sparingly soluble salts are calculated. The statistical meaning of G is discussed.

W. E. G.

Air Thermostat Regulated Electrically. HAJIME ISOBE (*J. Chem. Soc. Japan*, 1922, **43**, 650—653).—A description with diagram of an air thermostat regulated electrically, using as the source of heat an electric lamp, with Ikeda's regulator and relay. It is suitable for rather high temperatures (even above 80°), its accuracy being 0·05°. K. K.

Boundary Lubrication and Chemical Constitution. The Optically Active Carbinols of the Formula

$$C_2H_5{\cdot}CH(OH){\cdot}C_nH_{2n+1}.$$

IDA DOUBLEDAY (T., 1922, **121**, 2875—2879).

Surface Tension of Solid Substances. G. N. ANTONOFF (*Z. physikal. Chem.*, 1922, **102**, 388—392; cf. A., 1918, ii, 437).—In a previous paper (*loc. cit.*), the author has shown that the surface tension of a liquid may be deduced from a knowledge of the internal pressure by means of the equation $P=2\alpha\{(d-d_2)/M\}^{\frac{1}{3}}$, where P is the internal pressure, α the surface tension, d the density of the liquid, d_2 that of the saturated vapour, and M the molecular weight. In the present paper, on similar hypotheses, the author determines the vapour tension of solid substances. The weight required to cut through a piece of a solid is determined and from

this quantity the internal pressure is ascertained. A piece of rock salt is prepared 15 sq. mm. in cross section and 2—3 cm. long, and cut through by a wire to which a suitable load is attached. It is found that the force required to cut the crystal is a measure of the internal pressure and is the same in all three axial directions, and the surface tension has the value 3500 dyne/cm. This value is of the same order as that found by Ostwald (A., 1900, ii, 712) and Hulett (A., 1901, ii, 493) for barium and calcium salts. The above result is in accordance with some aspects of Bragg's symmetrical structure for this substance, but from other aspects a value about one thousand times as large might be anticipated.

J. F. S.

Adsorption and the Corresponding States. RICHARD LORENZ and A. LANDE (*Z. anorg. Chem.*, 1922, **125**, 47—58).—A theoretical paper in which the conclusions of Eucken (A., 1914, ii, 433; 1922, ii, 262) are discussed. The present authors claim that adsorption phenomena can be employed to calculate the dipolar moment of the adsorbed molecules. They explain the apparent independence of the adsorption potential on the temperature by assuming that the bulk of the adsorbed substance is concentrated on the adsorbing surface and that the orientating tendency of the adsorption force is much greater than the kinetic force produced by a higher temperature. In the regions where Henry's Law is obeyed, it is shown that the amount of gas adsorbed divided by its critical temperature is the same for all gases except hydrogen. The constant is equal to about 13; this is a strong argument for the identity of adsorption and molecular cohesion forces.

W. T.

Adsorption on Metal Surfaces. H. VON EULER [with E. G. RUDBERG] (*Z. Elektrochem.*, 1922, **28**, 446—449; cf. A., 1922, ii, 822).—Measurements have been made of the adsorption of the silver-ion from solutions of silver nitrate by gold and silver foil. Typical adsorption isotherms are obtained giving a maximum adsorption on a gold surface of 5·5 mg. silver per m^2., and on silver 8·5 to 9·0 mg. silver per m^2. Polished and etched surfaces gave the same amount of adsorption. Assuming the formation of a unimolecular layer, the atomic diameter of the adsorbed silver-ions was found to range from 1·4 to $1{\cdot}8\times10^{-8}$ cm. These values are smaller than that of Lorenz for the diameter of the silver-ion ($2{\cdot}8\times10^{-8}$ cm.), and that of Vegard from crystal measurements ($4{\cdot}06\times10^{-8}$ cm.). These divergences may be due to irregularities of the metal surface, and, on this view, the amount of adsorbed silver-ion can be used as a measure of the degree of roughness of the metal surface.

W. E. G.

Dissociation of Iodine Vapour and the Chemical Constant of Monatomic Iodine. H. BRAUNE and H. RAMSTETTER (*Z. physikal. Chem.*, 1922, **102**, 480—503).—With the object of bringing the experimentally determined chemical constant of iodine into

line with that calculated by means of the formula $C=-1\cdot59+1\cdot5 \log A$, the authors have redetermined the dissociation of iodine over the temperature range 600—1000°. The measurements were effected in a quartz flask and the pressure measurements were made by means of a new quartz thread manometer, which is capable of reading to 0·001 mm. The following values of the degree of dissociation are recorded for the given temperatures, which are expressed in absolute degrees: 945·8°, 0·2047; 991·0°, 0·2879; 1096·8°, 0·5228; 1226·8°, 0·7679; and 1343·8°, 0·8808. The results do not effect the experimental chemical constant as was hoped, and it is shown that an agreement between the theoretical value and the experimental value can only be brought about by the discovery of an unexpectedly large error in the heat of vaporisation of iodine and in the value, $\beta\nu=106$, which represents the change of the specific heat of solid iodine with temperature. J. F. S.

Dissociation of Hydrogen Sulphide, Sodium Sulphide, and Sodium Hydrosulphide in Aqueous Solution. KARL JELLINEK and JOHANNES CZERWINSKI (*Z. physikal. Chem.*, 1922, **102**, 438—479).—The depression of the freezing point, the electrical conductivity, and the *E.M.F.* of solutions of hydrogen sulphide, sodium sulphide, and sodium hydrosulphide have been measured at 0°, 18°, and 25° over a wide range of concentrations. The concentration of the various ions in the hydrolysis equilibrium of sodium sulphide and sodium hydrosulphide has been evaluated, and the following quantities have been obtained: Sodium sulphide, $0\cdot1N$ contains Na_2S, 0·0003, NaS′, 0·002, Na˙, 0·08, S″, 0·006, OH′, 0·035; SH′, 0·033, H˙ 30×10^{-15}, NaOH, 0·004, NaSH, 0·0055; sodium hydrosulphide $0\cdot1N$, NaSH, 0·085, S″, $3\cdot2\times10^{-6}$; H˙, $6\cdot3\times10^{-11}$; OH′$=H_2S$ $8\cdot0\times10^{-5}$, all expressed in normality. The degree of hydrolysis of the same substances has been calculated for various concentrations at 0°, and the following values have been obtained: Sodium sulphide $0\cdot1N$, 0·805, $0\cdot21N$, 0·754, $0\cdot53N$, 0·655, $1\cdot06N$, 0·585, $1\cdot59N$, 0·535, $2\cdot12N$, 0·50, and $2\cdot85N$, 0·46; sodium hydrosulphide $0\cdot1N$ 0·15% at 0° and 0·08% at 10°. It is shown to be probable that the temperature coefficient of the hydrolysis of sodium sulphide and of the heat of hydrolysis are small and the heat of dissociation of HS′ is large, about 13,000 cal. The first dissociation constant of hydrogen sulphide at 0° is found to be 1×10^{-7}, and the second dissociation constant 2×10^{-15}. From the great difference between the two dissociation constants and the heat of dissociation, it is shown that hydrogen sulphide must possess a strongly asymmetric structure. The dissociation of sodium hydrosulphide has been investigated at a number of temperatures. The mobility of the ions HS′ and S″ and their dependence on temperature have been ascertained. The following values are recorded: SH′; 0°, 42·5, 18°, 56·5°, and 25°, 64 all at infinite dilution. The solubility product of copper sulphide, silver sulphide, and lead sulphide have been determined, and the values Ag_2S. 3×10^{-50}, CuS, 3×10^{-42}, and PbS, 3×10^{-13} obtained. It is also shown that a more soluble form of lead sulphide exists. J. F. S.

The Diffusion of Acids in Aqueous Solution. L. W. OHOLM (*Finske Kemistamfundets Medd.*, 1921, **30**, 69—78).—From experiments conducted at 18—20° (±0·25°), the following values of the diffusion coefficient, *k*, corrected to 20°, are calculated. For nitric acid, 2*N*, 2·150; 1·5*N*, 2·141; *N*, 2·164; 0·5*N*, 2·227; 0·1*N*, 2·246; 0·05*N*, 2·266. For sulphuric acid, 2*N*, 1·297; 1·5*N*, 1·350; *N*, 1·369; 0·5*N*, 1·399; 0·1*N*, 1·498. For phosphoric acid, 3*N*, 0·644; 2*N*, 0·656; *N*, 0·692; 0·25*N*, 0·772. For boric acid, 1·5*N*, 0·813; *N*, 0·816; 0·5*N*, 0·826; 0·1*N*, 0·876; 0·05*N*, 0·954. For oxalic acid, 2*N*, 0·790; *N*, 0·875; 0·5*N*, 0·987; 0·1*N*, 1·215. For succinic acid, *N*, 0·604; 0·5*N*, 0·654; 0·1*N*, 0·708.

CHEMICAL ABSTRACTS.

The Influence of Salts on the Rate of Diffusion of Acid through Collodion Membranes. JACQUES LOEB (*J. Gen. Physiol.*, 1922, **5**, 255—262).—If a collodion membrane separate two solutions of hydrochloric acid of the same P_H, one of which contains a salt, for example, sodium chloride, there is observed along with the diffusion of the sodium chloride a temporary increase in the P_H of the liquid which originally contained no salt. This is explained as due to hydrogen-ions being carried along with the chlorine-ions in preference to the more slowly moving sodium-ions. This view is verified by the fact that the rate of diffusion of hydrochloric acid is increased by a salt. W. O. K.

Separation of Crystalloids by Dialysis. LOUIS KAHLENBERG (*Science*, 1921, **53**, 143).—Separation of the following pairs of substances was effected by dialysis, using pyridine as the solvent, and vulcanised caoutchouc membranes as the septa: (1) sucrose and sulphur, (2) silver nitrate and naphthalene, (3) silver nitrate and camphor, (4) silver nitrate and sulphur, (5) sucrose and camphor, (6) sucrose and naphthalene, (7) lithium chloride and sulphur, (8) lithium chloride and camphor, (9) lithium chloride and naphthalene, the first-named substance remaining in each case in the solution in the dialyser. It has also even been found possible to separate crystalloids from colloids by causing the latter to pass through the membrane. A. A. E.

Complex Compounds. A. MAGNUS (*Z. anorg. Chem.*, 1922, **124**, 289—321).—A theoretical paper (cf. A., 1922, ii, 559). Since the most stable complex is the one formed from its components with the greatest liberation of energy, the author shows that comparatively small central atoms have generally a low co-ordination number. The solubility of an inorganic compound is shown to depend on the dielectric constant and the dipolar moment of the molecules of the solvent. The author discusses qualitatively the solubility of a series of compounds from this point of view (cf. Fajans, *Naturwiss.*, 1921, **37**, 2). W. T.

The Significance of Crystal Structure. A Lecture delivered before the Chemical Society on October 26th, 1922. SIR WILLIAM H. BRAGG (T., 1922, **121**, 2766—2787).

Crystal Structure and Chemical Constitution. W. Grahmann (*Z. Kryst. Min.*, 1922, **57**, 48—93; from *Chem. Zentr.*, 1922, iii, 689—690).—Theoretical. It is maintained that the distinction between atom-lattices and molecule-lattices is purely formal, since the geometrical resolution of molecules in the crystal lattice does not involve a loosening of chemical valencies. Crystal structure is determined by the arrangement of atoms in the lattice and by the atom symmetry deduced from the total symmetry. Atomic symmetry is understood, not as a definite geometrical property of the atom, but as differing according to the arrangement of the valency electrons from compound to compound. The structure of the sodium chloride lattice and the influence of valency on the crystal structure of elements are discussed. The structure of typical metals is held to be mainly governed by the tendency to spherical packing, and not by valency electrons. Valency electron linking is correlated with anisotropy and electrical conductivity.

G. W. R.

Lattice Energy and Work of Ionisation of Inorganic Compounds. H. G. Grimm (*Z. physikal. Chem.*, 1922, **102**, 504—506; cf. A., 1922, ii, 690).—On the basis of some new wave-length measurements of Lyman (A., 1922, ii, 674) in which it appears that all helium terms are 0·8 volt=18·4 Cal. too large, the author has recalculated many of his results recently published. A list of the essential corrections to be applied to the previous values (*loc. cit.*) is given.

J. F. S.

Valencies which Stabilise the Crystal Lattices of Elementary Substances and of Compounds between Metals. M. Padoa (*Gazzetta*, 1922, **52**, ii, 189—202).—The author discusses the evidence bearing on the nature of the valencies by means of which crystals of metals and metalloids are constructed. The suggestion that these valencies have the significance of primary chemical valencies is open to serious objection. The behaviour of metals during anodic attack indicates that, in their crystalline space lattices, metals either exhibit a diminished valency or, more probably, are non-valent, like the rare gases. The peculiar position of carbon among the elements is maintained also in this respect, as it crystallises by means of its principal valencies (cf. A., 1919, ii, 96). As regards elements such as selenium, antimony, and arsenic, which are both non-metallic and metallic in character, it may be assumed that, in the non-metallic forms, the molecules are formed by means of principal valencies and are polarised, whereas in the metallic modifications these elements are non-valent and are united in the lattices by secondary valencies; the hypothesis that the non-metallic forms contain ions is supported by the fact that molecules like Cl_2, Br_2, and I_2 are auto-dissociated, although in small measure, and hence conduct electrolytically in the liquid state.

Isomorphism between metallic elements of one and the same group is regarded as due to the analogies between the non-valent

forms of these elements dependent on equality of the numbers and directions of the secondary valencies causing the stability of the crystal lattices. The formation of compounds between metals is capable of explanation on similar lines, the secondary valencies utilised in the construction of the crystal lattices being employed here also. The variation in the properties of alloys without corresponding variation in the composition is regarded as dependent on the existence of isomerism in the crystal lattices.

The question of the terminal elements of the lattices and their influence on stoicheiometric relations and on surface affinity is also discussed. In colloidal precipitates which are often ultramicroscopic but of crystalline structure, stoicheiometric relationships hold exactly, as is shown by the fact that copper, zinc, mercury, etc., may be estimated as sulphides. The external zone of the lattice, completed by the number of atoms of a given kind to yield simple, rational relations, exhibits secondary valencies which may serve to explain the phenomena of absorption and catalysis. Various crystallised substances exist which may be regarded as compounds of variable composition. Thus the compositions of minerals of the pyrrhotite group correspond with formulæ lying between Fe_5S_6 and $Fe_{16}S_{17}$. The excess of sulphur has been attributed to the formation of solid solutions of pyrites in ferrous sulphide, but it may depend on a microcrystalline structure with a granulation varying in different specimens and with incomplete polygons.

[With B. ZANELLA.]—The results of experiments on the anodic attack of mineral arsenides and sulpho-arsenides, of copper arsenides of the formulæ As_2Cu_5 and $AsCu_3$, and of copper–zinc alloys, are given in confirmation of the above views. T. H. P.

The Absolute Sizes of certain Univalent Ions. WHEELER P. DAVEY (*Physical Rev.*, 1921, **18**, 102—104).—Bragg's results, although consistent among themselves, are not in accord with experimental investigations on the crystals. In agreement with Langmuir's deductions (A., 1919, ii, 328), it is assumed that potassium, rubidium, and cæsium ions are equal in size to those of chlorine, bromine, and iodine, respectively, the values obtained being 1·56 Å., 1·73 Å., and 1·98 Å. The figures for sodium and fluorine ions are 1·25 Å. and 1·13 Å., respectively. A. A. E.

Quantitative Experiments on the Coagulation of Colloids. RAY V. MURPHY and J. H. MATHEWS (*Science*, 1921, **53**, 581).—Determinations of the lowest concentration (limiting concentration) of electrolytes necessary to coagulate hydrous ferric oxide sol show (1) that the limiting concentration decreases with increasing purity in the case of chloride-, chromate-, and ferricyanide-ions, the mechanism of the process being evidently similar for the three ions, (2) that the limiting concentration decreases markedly with decreasing concentration of the sol in the case of all three ions. The relation indicated by Burton and Bishop (A., 1921, ii, 176) for mastic, arsenious sulphide, and copper sols holds for ferric oxide hydrosol only in the case of the tervalent ion. A. A. E.

Silver Soap Gels. G. Stafford Whitby (*Science*, 1921, **53**, 580—581).—Silver salts of the fatty acids are capable of giving reversible gels in organic liquids, particularly in homologues of benzene, and in the halogenated derivatives of benzene and its homologues. The silver salts form gels at a lower point in the series of saturated fatty acids than do the alkali metal salts. The silver salts of the higher members of the saturated fatty acid series show a greater solvation capacity than those of the lower ones. Silver oleate gives a gel in benzene. In the case of solvents of the same general chemical character, the higher the boiling point of the solvent, the greater appeared to be the solvation capacity of a given salt, and the smaller the extent to which the gel from a given salt suffered syneresis. A. A. E.

Esterification by Silica Gel. C. H. Milligan and E. Emmet Reid (*Science*, 1921, **53**, 576).—Silica gel is more than twice as active as titanium oxide as a catalyst for esterification. A mixture of acetic acid and ethyl alcohol, when passed slowly at 150°, gives a percentage esterification of 75—80, instead of 67, which was previously regarded as the limit. A. A. E.

The Preparation of Active Nickel for Organic Catalysis. André Brochet (*Compt. rend.*, 1922, **175**, 816—819).—Three different methods of preparation of catalytic nickel for hydrogenation are described, and it is stated that the three varieties obtained have sensibly the same catalytic properties (see *J.S.C.I.*, 1923, Jan.). H. J. E.

Catalytic Decomposition of Hydrogen Peroxide by Ferric Salts. J. Duclaux (*Bull. Soc. chim.*, 1922, [iv], **31**, 961—966).—The work corroborates and complements that of von Bertalan (A., 1920, ii, 614) and Bohnson (A., 1921, ii, 250). For a constant concentration of iron, the reaction constant is found to be proportional to the hydrogen-ion concentration, provided that the latter has a value of $0{\cdot}003N$ and upwards. The inference is drawn that hydrogen peroxide behaves as a weak acid; its dissociation is thus reversed in presence of strong acid, and so the proportionality found would be expected on theoretical grounds. The lesser catalytic activity of ferric sulphate is explicable on the grounds of its smaller electrolytic dissociation and the results obtained on the addition of other ionogens (Bohnson, *loc. cit.*) are consistent with this explanation. The limiting value of hydrogen-ion concentration below which the reaction constant decreases is due to hydrolysis of the ferric salt in solutions where the value is lower with consequent diminution of its activity (cf. Tian, A., 1921, ii, 439). The general conclusion is drawn that all the experimental evidence tends to show that the reaction takes place between ferric-ions and HO_2-ions derived from the peroxide. H. J. E.

Catalytic Effect in the Reaction between Ketones and Halogens in Aqueous Solution. F. O. Rice (*Science*, 1921, **53**, 581).—Since higher ketones have the same velocity constant as acetone, and since, contrary to Lapworth, the reaction is accel-

erated by neutral salts, Lapworth's views (T., 1904, 85, 30) on the mechanism of the reaction are considered to be probably incorrect. A. A. E.

Forces within a Static Atom. IRVING LANGMUIR (*Physical Rev.*, 1921, **18**, 104).—If in addition to the Coulomb forces between charged particles the existence is assumed of another force (quantum force) $Fq=(1/mr^3)(nh/2\pi)^2$ acting between an electron and a nucleus, it is found that when a stationary electron is in stable equilibrium its distance from a nucleus, and its total energy, are in accord with Bohr's theory, and its frequency of oscillation about the position of equilibrium is identical with the frequency of revolution of the electron in the Bohr atom. Thus the Rydberg constant and the Balmer series can be deduced without the assumption of moving electrons. For the construction of models of the helium atom and hydrogen molecule, it is assumed that each electron acts towards the nucleus like a dipole acting on a charge, whilst the quantum action between electrons is like that between dipoles. The forces therefore depend on the orientation of the electrons as well as on their distance. It may be that each change in the quantum number associated with an electron corresponds with a change in the structure of the electron. A. A. E.

Atomic Systems based on Free Electrons, Positive and Negative, and their Stability. R. HARGREAVES (*Phil. Mag.*, 1922, [vi], **44**, 1065—1105).—A theoretical paper suggesting an atomic scheme of which the characteristic feature is a structure consisting of two concentric rings, one of positive and the other of negative electrons. W. E. G.

Missing Elements in the Periodic Table. F. H. LORING (*Chem. News*, 1922, **125**, 309—311).—Certain features of the periodic table may be accounted for by assuming that atomic number differences are represented by one or two types of mathematical series. It follows that missing elements only exist in minute quantities, if at all. The table to which reference is made is a development of that constructed by Langmuir. H. J. E.

The Nature of the Multiple Carbon Linking. H. J. PRINS (*Ber.*, 1922, **55**, [*B*], 3437—3439).—Mainly a re-statement of the author's views (cf. A., 1914, i, 648; 1917, i, 685; 1918, i, 261) consequent on the recent publications of Fajans (A., 1922, ii, 818).

The energy of a substance containing a double carbon linking is considered to comprise (i) energy of linking which causes the double bond to be "stronger" than the single bond, and (ii) atomic energy which conditions the activity of the carbon atoms and the greater amount of which renders them more active than similar atoms in saturated compounds. H. W.

Determination of the Velocity of Filtration. ANNA STEINER (*Kolloid Z.*, 1922, **31**, 204—209).—The velocity of filtration of suspensions and colloidal solutions may be measured by the following method. The top of a burette is widened so that it

will take a cork through which the stem of a filter funnel passes, and a side tube is attached near to the top but just above the graduation. The side tube is connected through a manometer and safety flask with a water pump and a definite volume of the suspension placed in the filter-paper. The volume of liquid collected in the burette is read at intervals and a filtration curve drawn. For quantitative work, the pressure of the filtration must be kept constant. The velocity of filtration is shown to change markedly with changes of hydration of the suspension and also with the presence of electrolytes. J. F. S.

Inorganic Chemistry.

The [Suggested] Formation of Helium and Neon in Geissler Tubes containing Hydrogen. ARNALDO PIUTTI (*Z. Elektrochem.*, 1922, 28, 452—453).—The author has varied the experimental conditions operating in Geissler tubes with a view to the production of helium and neon from hydrogen. In all, 70 different experiments were carried out, and variations were made in the size of the electrodes, their difference apart, the nature of the current, etc. In no case was found any trace of the D_3 line of helium, or of the D_5 line of neon, or any evidence of the conversion of hydrogen into neon or helium (cf. A., 1920, ii, 311). W. E. G.

Hydrogen as a Halogen in Metallic Hydrides. DWIGHT C. BARDWELL (*J. Amer. Chem. Soc.* 1922, 44, 2499—2504).—A new method is described for the preparation of pure sodium and potassium hydrides. Pure sodium or potassium was placed in a steel test-tube and heated to 400° by immersing in a eutectic bath of sodium and potassium nitrates. Pure hydrogen, made by passing electrolytic hydrogen through a tube containing platinised asbestos at 400°, two tubes containing phosphoric oxide, and finally bubbling through sodium potassium eutectic alloy, was passed into the molten metal by a steel tube, when the hydride formed in fine, white crystals higher up the test tube where it was scraped into glass side tubes and sealed up. Calcium hydride free from metallic calcium was similarly prepared in the form of white crystals. The absence of free metal in the above-named compounds was demonstrated by leaching with liquid ammonia, which remained quite colourless. Solutions of the hydrides in a molten eutectic mixture of potassium and lithium chloride were electrolysed, when it was found, chiefly in the case of calcium hydride, that hydrogen was liberated at the anode in quantities strictly in keeping with Faraday's law, whilst no gas was liberated at the cathode. J. F. S.

Improved Still for Producing Pure Water. CHARLES A. KRAUS and WILBUR B. DEXTER (*J. Amer. Chem. Soc.*, 1922, 44, 2468—2471).—Water having a specific conductivity of $0{\cdot}12\times10^{-6}$

ohms^{-1} may be obtained in large quantities by the use of a still constructed as follows. A copper boiler of 90 litres capacity is connected at the top with a block tin tube, which leads to a tinned copper chamber containing a filter of asbestos fibre or glass wool between two pieces of nickel gauze. The steam passes through the filter and a portion condenses and runs off through a drip tube. The residue of the steam passes into a settling chamber, also of tinned copper, and thence to a block tin worm in which the water is condensed. Water having a specific conductivity $0{\cdot}05\times10^{-6}$ ohms^{-1} at 18° may also be prepared in quantity. The principle on which the preparation depends consists in allowing about 20% of the steam to pass away uncondensed. This carries with it practically all the carbon dioxide and other volatile impurities present in the water. The still used in this case is a copper boiler as before, connected directly by a block tin pipe to the settling chamber. From this the steam passes through a block tin pipe, which at its lower end is surrounded by a condenser jacket, to a separating chamber where a large fraction about 70—80% of the water condenses and runs away; the residual 20% of the steam carrying all the volatile impurities escapes from the top of the separating chamber. In both the above cases ordinary distilled water is placed in the boiler and this is made alkaline with sodium hydroxide and a little potassium permanganate is added. When not in use, the water in the boiler is kept near to the boiling point so that air is not dissolved in it to any large extent. J. F. S.

Structure of Molecules of Water. IRVING LANGMUIR (*Science*, 1921, **53**, 580).—In view of Dennison's demonstration (*Physical Rev.*, 1921, **17**, 20) that ice consists of molecules of the formula H_4O_2, a structure is proposed in which the four hydrogen nuclei bind the two oxygen atoms. The duplet held by each hydrogen nucleus has one of its electrons in each of the oxygen octets, instead of the more usual arrangement in which both electrons of a duplet form part of the same octet. A. A. E.

Properties of Pure Hydrogen Peroxide. III. O. MAASS and W. H. HATCHER (*J. Amer. Chem. Soc.*, 1922, **44**, 2472—2480; cf. A., 1921, ii, 106).—A continuation of previous work in which the properties of pure hydrogen peroxide have been investigated. It is shown that hydrogen peroxide is diamagnetic and has a susceptibility of $8{\cdot}8\times10^{-7}$, a value which is larger than that of water. This may be taken as evidence in favour of a structure for hydrogen peroxide in which the oxygen atoms are not connected in the same way as in the oxygen molecule. The solubility of anhydrous hydrogen peroxide has been measured in a number of organic solvents with the following results at 0°. Benzene is quite immiscible, alcohol completely miscible, and ether partly miscible. The solubility curves of sodium chloride, sodium nitrate, sodium sulphate, and sucrose in anhydrous hydrogen peroxide have been determined, and it is shown that the degree of dissociation is of the same order as in water. The tendency toward the formation of molecular compounds is less than in the case of water, there

being evidence of only one compound, namely, $Na_2SO_4,2H_2O_2$. The action of the halogen hydrides on pure hydrogen peroxide and its aqueous solutions has been examined and the conditions have been determined under which the oxidation of the haloid occurs. These are to form the subject of a future paper. The halogens are found to be less soluble in hydrogen peroxide than in water. Ammonia dissolves in pure hydrogen peroxide, with the formation of a crystalline compound which melts at 24·5° and is stable in the absence of water. This compound is slightly soluble in ether, and may be formed by passing ammonia into an anhydrous solution of the peroxide in ether. A compound of the formula $2NH_3,H_2O_2$ was not obtained. The stability of the compound NH_3,H_2O_2 shows that it is the hydroxyl-ion which causes the decomposition of hydrogen peroxide. Water dissociates or possibly hydrolyses it, and, with the consequent formation of hydroxyl-ions, the decomposition is cumulative. Whether or no this compound is an ammonium salt, NH_4O_2H, is not certain. The vapour pressure, dielectric constant, and conductivity of salts in hydrogen peroxide are under investigation, and the results will be published shortly.

J. F. S.

Activation of Chlorine. GERALD L. WENDT, ROBERT S. LANDAUER, and W. W. EWING (*J. Amer. Chem. Soc.*, 1922, **44**, 2377—2382).—A number of methods have been used in an attempt to activate chlorine, but neither the light from a 3000-watt Bovie mercury lamp nor a high potential electric discharge was found capable of converting chlorine into an active form such that it would react with hydrogen in the dark. The experiments described by Draper (*Phil. Mag.*, 1843, [iii], **23**, 491; 1848, **25**, 9, 1845; **26**, 473; **27**, 327) have been repeated and confirmed. It is shown that the fact that the latent period in the hydrogen–chlorine reaction can be destroyed by previous insolation of the chlorine must be attributed to the destruction of substances which inhibit the reaction rather than to any activation of the chlorine itself. J. F. S.

Preparation of Pure Ozone and Determination of its Molecular Weight. SEBASTIAN KARRER and OLIVER R. WULF (*J. Amer. Chem. Soc.*, 1922, **44**, 2391—2397).—Pure ozone may be prepared by leading the gas issuing from an ozoniser into a bulb condenser cooled with liquid air until the bulb in which the liquid mixture is collected is about one-half to three parts filled with the deep blue liquid mixture of ozone and oxygen. In this process, a considerable concentration may be obtained by periodically lifting the condenser from the liquid air and so effecting a partial condensation only. The mixture is then distilled at −182°, when for a long period oxygen containing only 0·8% of ozone passes off, that is, the distillation proceeds as though liquid oxygen and liquid ozone were immiscible. At the temperature stated, liquid ozone has a vapour pressure of 6 mm. After distillation has been carried on for some while and most of the liquid has passed off and the residue is very small in volume, the temperature rises slowly to −110°, and then a blue gas, practically pure ozone, commences

to distil over. At this stage of the operations extreme care is necessary if explosions are to be avoided. After the blue gas has distilled over for some time, it becomes much darker in colour and this gas, which is pure ozone, was collected in a globe of known volume. The pressure of the gas in the bulb, the weight, and the pressure after decomposing the ozone by heating to ordinary temperature were determined and the molecular weight was calculated. As a mean of many experiments, the value 47·3 was obtained. It is shown that there is no evidence to confirm the existence of tetratomic and hexatomic allotropes of oxygen.

J. F. S.

The Polythionic Acids. F. FOERSTER and A. HORNIG (*Z. anorg. Chem.*, 1922, **125**, 86—146).—The reaction between sulphurous acid and hydrogen sulphide can be represented by the equilibrium $H_2S+H_2SO_3 \rightleftharpoons H_2S_2O_2+H_2O$. Further reaction with hydrogen sulphide produces sulphur, whereas excess of sulphurous acid leads to the formation of pentathionic acid. Of the polythionic acids and their alkali salts, the tetrathionates are the most stable, and the trithionates the most unstable; the pentathionates occupy a mean position. None of these compounds is completely stable in aqueous solution, the following decompositions taking place: $S_5O_6'' \rightleftharpoons S_4O_6''+S$. $S_4O_6'' \rightleftharpoons S_3O_6''+S$. $S_3O_6''+H_2O=SO_4''+S_2O_3''+2H^{\cdot}$. $S_2O_3''+H^{\cdot} \rightleftharpoons HSO_3'+S$. The insolubility of sulphur removes it from the equilibrium, and at boiling temperature the sulphur dioxide is removed and SO_4'' is alone left in solution; side reactions were also found to take place. The more sulphur dioxide and sulphur there remains in the solution, the greater is the tendency of thiosulphuric acid to polymerise, *e.g.*, $S_3O_6''+S_2O_3''H^{\cdot} \rightleftharpoons S_4O_6''+HSO_3'$. $S_4O_6''+S_2O_3''+H^{\cdot} \rightleftharpoons S_5O_6''+HSO_3'$. A high concentration of hydrogen-ion retards the decomposition of tetra- and penta-thionic acids, but not of trithionic acid.

W. T.

Specific Volume of Liquid Ammonia. C. S. CRAGOE and D. R. HARPER (*U.S. Bur. Standards, Sci. Papers*, 1921, **420**, 287—315).—The apparatus used in the determination of the specific volume of saturated liquid ammonia is described and the results obtained for every degree from −70° to 100° are tabulated. These may be expressed by the equation: $\mu=[4{\cdot}2830+0{\cdot}813055\sqrt{133-\theta}-0{\cdot}0082861(133-\theta)]/[1+0{\cdot}424805\sqrt{133-\theta}+0{\cdot}015938(133-\theta)]$ where μ is expressed in c.c. per g. and θ in °C. A. R. P.

Oxidation of Nitrogen Tetroxide by Ozone. OLIVER R. WULF, FARRINGTON DANIELS, and SEBASTIAN KARRER (*J. Amer. Chem. Soc.*, 1922, **44**, 2398—2401).—The oxidation of nitrogen tetroxide to nitrogen pentoxide by ozone has been investigated at 25°. The oxidation occurs almost instantaneously and in consequence a piece of apparatus has been constructed whereby the oxidation can be followed titrimetrically, using the disappearance of brown fumes as an indication of the end-point, thus carrying out a true titration in the gaseous phase. The results show that

one molecule of ozone is required to oxidise one molecule of nitrogen tetroxide at 25°, thus only one atom of the ozone molecule is available in the oxidation at this temperature. This result is in striking contrast to the oxidation of sulphur dioxide to the trioxide by ozone at temperatures below 40° in which one molecule of ozone oxidises three molecules of sulphur dioxide, all three atoms of the ozone molecule being available for oxidation. J. F. S.

Decomposition of Nitrogen Pentoxide in the Presence of Ozone. Farrington Daniels, Oliver R. Wulf, and Sebastian Karrer (*J. Amer. Chem. Soc.*, 1922, **44**, 2402—2404).—According to the experiments of Daniels and Johnston (A., 1921, ii, 249), nitrogen pentoxide decomposes rapidly at the ordinary temperature. It is shown that in the experiments on the oxidation of nitrogen tetroxide by ozone (preceding abstract) in which a trace of ozone in excess was present, a very long period of time elapsed before any visible decomposition of the pentoxide was observed. Calculations from Daniels and Johnston's results show that the brown colour ought to have returned to the gas in 15·3 minutes, but actually it was found that this did not happen until the gas had been kept at 80° for 195 minutes. It follows, therefore, that a trace of ozone retards the decomposition of nitrogen pentoxide. If traces of the decomposition products are added to the system the decomposition takes place with its normal velocity. J. F. S.

Cryoscopy of Boron Trifluoride Solutions. V. Systems with Methyl Ether and with Methyl Chloride. A. F. O. Germann and Marion Cleaveland (*Science*, 1921, **53**, 582).—The melting-point curve of boron trifluoride and methyl ether shows a eutectic at 3 mol. % of boron trifluoride, and a maximum at 50 mol. %, corresponding with the formation of the compound $BF_3,(CH_3)_2O$, previously prepared by Gasselin. The melting-point curve of boron trifluoride and methyl chloride shows two maxima, at 15 mol. % and 33 mol. %, respectively, of boron trifluoride, and an angular point in the curve at 50%. The form of the maximum at 15% is identical with that at 50% for methyl ether, and the mixture yields a compound having the same f. p. and b. p. as the compound $BF_3,(CH_3)_2O$. It appears that methyl ether may be present as an impurity in methyl chloride as a constant boiling mixture. The use of boron trifluoride for its detection is suggested. A. A. E.

Catalysis in the Interaction of Carbon with Steam and Carbon Dioxide. H. A. Neville and H. S. Taylor (*Science*, 1921, **53**, 577).—Potassium carbonate and other salts accelerate the interaction of carbon and steam, and carbon and carbon dioxide. Reduced nickel also markedly promotes interaction of carbon and carbon dioxide. It has been shown that adsorption of carbon dioxide by carbon at 445° is increased by addition to the carbon of such accelerating agents, although the latter themselves show no adsorptive property for the gas. A. A. E.

Vapour Density of Technical Phosgene. A. F. O. Germann and Vernon Jersey (*Science*, 1921, **53**, 581).—Pure carbonyl chloride has a vapour tension of about 552 mm. at 0°; technical phosgene, which contains impurities probably consisting of carbon dioxide and hydrogen chloride, gives after repeated fractionation a value for the vapour density of 4·5263 g. per litre (uncorr.).

A. A. E.

Cryoscopy of Carbonyl Chloride Solutions. I. System with Chlorine. A. F. O. Germann and Vernon Jersey (*Science*, 1921, **53**, 582).—The melting-point curve of solutions of carbonyl chloride and chlorine exhibits a eutectic point at 25 mol. % of chlorine, and angular points at 6%, 11%, 50%, 63%, 75%, and 91%, indicating the existence of the following compounds which dissociate at the melting point: $16COCl_2,Cl_2$; $8COCl_2,Cl_2$; $COCl_2,Cl_2$; $3COCl_2,5Cl_2$; $COCl_2,3Cl_2$; and $COCl_2,10Cl_2$. The mechanism of the catalytic preparation of carbonyl chloride from carbon monoxide and chlorine is briefly discussed. A. A. E.

The Identity of Amorphous and Crystalline Silicon. Wilhelm Manchot (*Z. anorg. Chem.*, 1922, **124**, 333—334).—The identity of amorphous and crystalline silicon has been proved by an *X*-ray examination carried out by Debye and Frauenfelder. The preparation and properties of the two forms have been given in previous papers (cf. A., 1922, ii, 144, 286, 764). They can also be distinguished by rubbing them with lead peroxide; nothing happens in the case of the crystalline variety, but the pseudo-amorphous forms ignite, the brown form exploding. The greater reactivity of the latter is due to its very fine state of division.

W. T.

Magnetic Analysis of Silicates and Silicic Acids. Paul Pascal (*Compt. rend.*, 1922, **175**, 814—816).—Three types of hydrated silicon dioxide were investigated magnetically, all of which behaved as a mixture of anhydrous oxide and water. The conclusion is drawn that definite silicic acids do not exist (cf. van Bemmelen, A., 1908, ii, 838; 1909, ii, 234; and Le Chatelier, A., 1908, ii, 1033). H. J. E.

The Reduction of Potassium Chlorate by Ferrous Sulphate. M. Herschkowitsch (*Z. anorg. Chem.*, 1922, **125**, 147—154).—A dry mixture of potassium chlorate and ferrous sulphate remains unchanged up to 100°; a trace of water causes the evolution of chlorine dioxide and chlorine. In very dilute solutions, the chlorate is completely reduced to the chloride. W. T.

Crystal Structures of Potassium Chloroplatinite and of Potassium and Ammonium Chloropalladite. Roscoe G. Dickinson (*J. Amer. Chem. Soc.*, 1922, **44**, 2404—2411).—Tetragonal crystals of potassium chloroplatinite and potassium and ammonium chloropalladite have been examined by *X*-ray methods, using photographs of spectra and symmetrical and unsymmetrical Laue photographs. The simplest structure which will account for

the *X*-ray data has been described. In this structure, each platinum or palladium atom is surrounded by four equidistant and equivalent chlorine atoms lying in one plane. The distance between the platinum atom and a chlorine atom in potassium chloroplatinite is 2·33±0·05 Å.U. It is further shown that the structure of the chloroplatinites is very closely connected with that of the cubic crystals of the chloroplatinates. The tetragonal structure is only slightly larger than the cubic one in its horizontal dimensions, but considerably shorter vertically. A table is given in which the dimensions of the salts under examination are compared with those of the chloroplatinates and chloropalladates. J. F. S.

The Hydrates of Sodium Sulphide. A. SANFOURCHE and (MLLE) A. M. LIEBAUT (*Bull. Soc. chim.*, 1922, [v], **31**, 966—972; cf. Sabatier, A., 1879, 865 and 866; Gottig, A., 1886, 980; Parravano and Fornaini, A., 1907, ii, 951).—A thermal study of the system sodium sulphide–water reveals or confirms the existence of three hydrates, $Na_2S,9H_2O$, $Na_2S,5{\cdot}5H_2O$, Na_2S,H_2O. The evidence for the existence of the last is less trustworthy than for the former two hydrates, the reason being that experimental difficulties hinder the investigation of the system under those conditions which render the hydrate stable. The monohydrate and nonahydrate both decompose at temperatures below their respective melting points. The hydrates Na_2S,H_2O and $Na_2S,5{\cdot}5H_2O$ appear to undergo transformation into each other in the solid state. Other hydrates which have been described are not detected in this method of investigation. H. J. E.

Sodium Silicate Crystals. ALFRED HEINRICH ERDENBRECHER (*Z. anorg. Chem.*, 1922, **124**, 339—354).—This investigation of the hydrates of sodium silicate was carried out by plotting the cooling curve of the fused salt. This on melting gives a viscous paste; it was therefore mixed with a little paraffin oil, the latter having no effect on the cooling curves of sodium carbonate and sodium sulphate. The following hydrates were obtained. $Na_2SiO_3,9H_2O$, rhombic, m. p. 47·0°; $Na_2SiO_3,6H_2O$, monoclinic, m. p. 62·5°; and $Na_2SiO_3,4H_2O$, hexagonal, m. p. about 85·0°. The hydrate $Na_2SiO_3,14H_2O$ probably exists also.

The concentration of the alkali determines which hydrate crystallises from an alkaline solution. W. T.

Crystal Structure [of Cæsium Chloride and Thallous Chloride]. WHEELER P. DAVEY and FRANCES G. WICK (*Physical Rev.*, 1921, **17**, 403—404).—Cæsium chloride is considered to be a simple cube of cæsium-ions with a chlorine-ion at the centre of each cube of side 4·12 Å. Thallous chloride is similarly constituted, the side of the cube being 3·85 Å. These results are inconsistent with those of Bragg. A. A. E.

The Crystal Structure of Ammonium Chloride. RALPH W. G. WYCKOFF (*Amer. J. Sci.*, 1922, [v], **4**, 469—475; cf. A., 1922, ii, 290).—The structure of the low temperature form of ammonium chloride, as determined from *X*-ray powder measure-

ments, is at variance with that deduced from a study of the face development and etch figure formation of this substance. Laüe photographic data have been obtained by the author, which are in agreement with the powder data in assigning one chemical molecule within the unit cube. The symmetry of the crystal as a whole must be hemimorphic, hemihedral (tetrahedral), or possibly holohedral, but in no case can the arrangement of the atoms of the crystal agree with the enantiomorphic hemihedry, which studies of face development and etch figures assign to it. The latter "chemical" means of deducing crystal structure supplies information with regard to surface of the crystal, and the internal structure of the crystal is only one of a number of factors which bear on the nature of these surface phenomena. W. E. G.

Spontaneous Decomposition of Ammonium Chlorate. FRED FAIRBROTHER (*J. Amer. Chem. Soc.*, 1922, **44**, 2419—2422).—About 30 g. of ammonium chlorate were kept in contact with 100 c.c. of its saturated solution at ordinary temperature; for about three weeks the salt remained white, whilst a small quantity of a colourless gas was evolved. Later, the gas became tinged with greenish-yellow and a slow but continuous evolution of gas occurred. By the beginning of the fifth week the solution had become quite yellow and the amount of solid had decreased and the rate of decomposition appeared to be increasing. The liquid gradually became darker and considerable quantities of "euchlorine" were evolved. The temperature rose to 30—40° and within a few hours the system exploded. Solutions of ammonium chlorate in the absence of the solid may be kept indefinitely without any decomposition. The solid residue obtained from the decomposition is ammonium nitrate. It is shown that the rate of decomposition of ammonium chlorate is autocatalytically accelerated when the products of decomposition are not quickly removed. The reaction is regarded as taking place as follows. In the initial stage a very slow autoxidation of the molecule is taking place with the production of nitric acid, nitrogen, chlorine, and water. The nitric acid reacts with more chlorate, producing chloric acid and chlorine dioxide. These then oxidise more of the ammonium radicle with the formation of more nitric acid and the liberation of chlorine. This takes place more rapidly than the initial stage and consequently the decomposition tends to increase in speed unless the acid gases are removed quickly. The more stable perchlorate does not appear to be formed. J. F. S.

Crystal Analysis of Metallic Oxides. WHEELER P. DAVEY and E. O. HOFFMAN (*Physical Rev.*, 1920, **15**, 333).—Calcium, magnesium, cadmium, and nickelous oxides form a face-centred cube of the metal, interpenetrating a similar face-centred cube of oxygen, so that the combined lattices form a simple cube of which the side is half that of the face-centred cube; the lengths of the side of this simple cube are 2·37 Å., 2·09 Å., 2·36 Å., and 2·10 Å., respectively. Alumina forms a rhombohedron, of which the

hexagonal axes each have a length of 4·86 Å., and the vertical axis 6·62 Å. A. A. E.

The Ammines of the Strontium Haloids. GUSTAV F. HÜTTIG (*Z. anorg. Chem.*, 1922, **124**, 322—332).—Octammine strontium chloride was degraded isothermally, constancy of pressure indicating the existence of compounds. The formation of the following ammines were thus proved: $[Sr(NH_3)_8]Cl_2$ (3·5°), $[Sr(NH_3)]Cl_2$ (45·5°), $[Sr(NH_3)_8]Br_2$ (30°), $[Sr(NH_3)_2]Br_2$ (68°), $[Sr(NH_3)]Br_2$ (146°), $[Sr(NH_3)_8]I_2$ (31°), $[Sr(NH_3)_6]I_2$ (74·5°), $[Sr(NH_3)_2]I_2$ (134°), $[Sr(NH_3)]I_2$ (204°). In brackets are given for each complex the temperature at which its dissociation pressure is equal to 100 mm. W. T.

Separation of the Isotopes of Zinc. ALFRED C. EGERTON (*Nature*, 1922, **110**, 773).—It has been found possible to separate zinc by fractional distillation into a distillate and a residue, the densities of which bear to that of the initial metal the ratios 0·99971 : 1 and 1·00026 : 1, respectively, the differences being greater than the probable experimental error. The change in the atomic weight implied by this separation is about 0·035, which is considerably less than might be expected if the metal was composed of equal quantities of an isotope of atomic weight 64, on the one hand, and of isotopes of atomic weight 66, 68, and 70, on the other. A. A. E.

Preparation of Zinc Nitride. W. J. BENTLY and PAUL L. STERN (*Science*, 1921, **53**, 143).—Ammonia, free from oxygen and moisture, is passed over zinc dust (previously washed with a solution of ammonia and ammonium chloride, alcohol, and ether, and dried in a vacuum) for thirty minutes at 650° and the product cooled to at least 200° before exposure to the air. The highest yield obtained was 36·8% of nitride. A. A. E.

The Extraction of Glucina (Beryllia) from Beryl. HUBERT THOMAS STANLEY BRITTON (*J. Soc. Chem. Ind.*, 1922, **41**, 349—352T).—Various methods for the separation of glucina and alumina have been reinvestigated with the object of developing, if possible, a method which could be worked for the isolation of glucina from beryl. Although this object has not been completely attained, it was found that more than 90% of the alumina can be easily separated from the glucina by crystallising out the former in the form of potassium alum under suitable conditions. The ore is ground to a flour and fused with potassium hydroxide. The ground product is treated with sulphuric acid and the precipitated silica separated. The filtrate containing the sulphates of glucinum, aluminium, and potassium with excess of sulphuric acid is adjusted to about 5*N*-acidity by addition of potassium hydroxide, as it was found that whereas the solubility of glucinum and aluminium sulphates and of alum are somewhat reduced in 5*N*-sulphuric acid, that of potassium sulphate is considerably increased, and an increase in the liquid phase of the proportion of potassium to the other sulphates causes an increased separation of alum. The

acid liquid is therefore saturated with potassium sulphate at the boiling temperature, and set aside to crystallise at 0°. The solid phase obtained under these conditions always consisted entirely of alum, and represented 92·9% of the alumina present in one of the experiments quoted where the molecular proportions of glucina to alumina were 3 : 1 as in beryl, and where 4 mols. of potassium sulphate were present in the solution for crystallisation. At 25°, 87·6% of the alumina was separated. The glucina was separated from the mother-liquor by adding sodium hydroxide sufficient to redissolve the precipitate, diluting and boiling, when glucinum hydroxide was precipitated. The paper contains full data and curves representing the solubility of potassium sulphate in sulphuric acid of various strengths. G. F. M.

Constitution of Aqueous Solutions of Thallium Salts. C. DRUCKER (*Z. Elektrochem.*, 1922, **28**, 463—467).—From measurements of the depression of freezing point and concentration potentials of solutions of thallous nitrate, it is shown that this salt gives rise on ionisation to appreciable quantities of $Tl_2^{\cdot\cdot}$-ions. Below $C=0·06$ molar, the solutions follow the simple Ostwald dilution law, and the association of $Tl^{\cdot}$ to $Tl_2^{\cdot\cdot}$ may be neglected. At higher concentrations, all the ionic equilibria obey the law of mass action, and for $2Tl^{\cdot} \rightleftharpoons Tl_2^{\cdot\cdot}$, $K=2·1$. For $TlNO_3 \rightleftharpoons Tl^{\cdot}+NO_3'$ $K=0·27$ for all of the concentrations investigated. The mobility of the complex thallium-ion is 110.

These data for the bivalent thallium-ion are in accord with the previous work on thallium sulphate solutions (cf. A., 1921, ii, 161). The interpretation of the conductivities of thallous salts is satisfactorily explained on the classical dissociation theory. The Ghosh theory of complete ionisation of electrolytes leads to erroneous results when applied to solutions of thallous nitrate. W. E. G.

The Structure and Chemical Activity of Copper Films, and the Colour Changes accompanying their Oxidation. C. N. HINSHELWOOD (*Proc. Roy. Soc.*, 1922, [*A*], **102**, 318—328).—The diffraction colours produced on a copper surface by oxidation become more intense as the surface increases in chemical activity. After repeated oxidation and reduction, the permanent colour sequence is purple, blue, green, light green (almost yellow), purple, blue, black, and this order of colours may be traversed time after time. The film of copper which is formed in this manner is composed, according to Beilby, of small discrete units giving an "open formation" or granular structure. These granules are shown by the author to possess an order of magnitude less than 1 μ. The extent to which these granules are converted into oxide determines the colour of the diffracted light, the colour phenomenon being independent of the thickness of the film. Thus when the granules are one-third copper oxide and two-thirds copper, the colour of the scattered light is bright blue. No diffraction effects occur during the reduction of the oxide. The reduction phenomena are in agreement with the view that fresh nuclei of copper grow at the

expense of the oxide nuclei. After repeated treatment, the copper film becomes incapable of further sub-division, and a limiting velocity of oxidation is attained. W. E. G.

Phenomena of Diffusion in Metals in the Solid State and Cementation of Non-ferrous Metals. III. Influence of the Vapour Pressure of the Migratory Elements in the Formation of the Superficial Cementated Layer. G. Sirovich and A. Cartoceti (*Gazzetta*, 1922, **52**, ii, 233—245).—The cementation of copper by means of ferro-manganese or chromo-manganese (cf. A., 1922, ii, 68, 571) consists first of the formation at the surface of the bar of a layer of alloy containing the migratory element in definite concentration and secondly of the flow of this element into the interior of the bar. The authors explain the first stage of the process on the assumption that, at the experimental temperature employed, the cementated material exhibits a certain vapour or dissociation pressure in the various elements constituting it, so that the medium in which the material to be cementated may, after some time, be regarded as saturated as regards the vapours of these elements. This idea is developed, and the results of further experiments are brought into conformity with it. T. H. P.

Phenomena of Diffusion in Metals in the Solid State and Cementation of Non-ferrous Metals. IV. Cementation of Copper by means of Ferro-aluminium. G. Sirovich and A. Cartoceti (*Gazzetta*, 1922, **52**, ii, 245—249; cf. preceding abstract).—Cementation of copper by means of aluminium, like that by means of manganese, may result in the penetration of the metal to considerable depths and by relatively high proportions of the migrating metal. T. H. P.

Relation between Colour and Texture of Alloys. Masumi Chikashige (*Z. anorg. Chem.*, 1922, **124**, 335—338).—Copper reflects red to orange-yellow light, the addition of tin gives a white alloy, and the whiteness reaches a maximum when the composition corresponds with Cu_3Sn. The colour then gradually assumes the colour of tin, which only reflects light from red to the beginning of blue. W. T.

Catalysis in the Reduction of Oxides and the Catalytic Combination of Hydrogen and Oxygen. R. N. Pease and H. S. Taylor (*Science*, 1921, **53**, 577).—Oxygen and water vapour, when present in hydrogen used for the reduction of copper oxide, markedly inhibit the reaction, whilst the addition of reduced copper to the oxide appears to accelerate the reaction. The induction period in the reaction is attributed (*a*) to initial drying of the oxide, (*b*) to slow initial formation of copper, which then acts as a catalyst. The mechanism of the catalytic combustion of hydrogen and oxygen in presence of copper is briefly discussed. A. A. E.

Separation of Isotopes by Distillation and Analogous Processes. ROBERT S. MULLIKEN (*J. Amer. Chem. Soc.*, 1922, **44**, 2387—2390).—A continuation of previous work on the separation of the isotopes of mercury. It is shown that the separation coefficient of mercury is 0·0063, and not 0·0057 as previously stated (A., 1922, ii, 295). The progress of the separation has been followed by means of density determinations. The effect of various factors, such as pressure, rate of distillation, and form of the apparatus, on the efficiency of separation of isotopes by the method of non-equilibrium distillation has been studied, and it is shown that an efficiency of 50% is readily attained. A film of dirt on the mercury increases the efficiency at the higher rates of distillation. It is pointed out that irreversible distillation may be applied as a new factor in the separation of non-isotopic liquid mixtures. The failure of attempts to secure a separation of the isotopes of mercury by electrolytic solution or by reaction with sulphur is ascribed to the great difficulty of obtaining non-equilibrium conditions at the boundary between two condensed phases. J. F. S.

Potassium Ammonioaluminate and Ammoniomanganite. FRANCIS W. BERGSTROM (*Science*, 1921, **53**, 578).—*Potassium ammonioaluminate*, $Al(NH_2)_2{\cdot}NHK$, has been prepared by the action of potassamide in liquid ammonia solution on amalgamated aluminium, and *potassium ammoniomanganite*, $Mn(NHK)_2,2NH_3$, by the action of an excess of potassamide on manganese thiocyanate. A. A. E.

The Growth of the Grains in Unworked Iron and the Appearance of a Striated Structure after Heating it at more than 1100°. KARL DAEVES (*Z. anorg. Chem.*, 1922, **125**, 167—172).—Iron which contains but a small amount of carbon assumes a new structure on being heated at 1125°; this is due to the separation of ferrite and pearlite in certain directions which are orientated crystallographically. Rapid cooling results in the incomplete separation of pearlite. This structure is closely associated with the development of coarse grains, and the iron is deteriorated; it can be overcome by heating at 900°. W. T.

Complex Phosphato- and Arsenato-metal Acids. L. DEDE (*Z. anorg. Chem.*, 1922, **125**, 28—46).—The addition of phosphoric acid solution to a ferric chloride solution results in a considerable increase in the specific conductivity of the solution; the latter also increases rapidly with the further addition of the acid solution and reaches a constant value when equivalent amounts of salt and acid are mixed. This is assumed to be due to the formation of the complex trichlorophosphatoferric acid, $[Cl_3Fe(PO_4)]H_3$. This complex acid could not be isolated; the same applies to its salts. Further addition of phosphoric acid solution, whilst having no appreciable effect on the conductivity, resulted in the replacement of the three chlorine atoms of the complex by another phosphato-group, *i.e.*, *diphosphatoferric acid;* this was isolated and analysed; it corresponds with $[Fe(PO_4)_2]H_3+2\frac{1}{2}H_2O$. The complex is very stable, and the author points out its application to

analysis. Arsenic acid gave analogous compounds. Aluminium and glucinum salts also show a considerable increase in specific conductivity on being mixed with a solution of phosphoric acid. These are being further investigated. W. T.

Behaviour of the Stannic Acids towards Solutions of Alkaline Hydroxides. GEORGE ERNEST COLLINS and JOHN KERFOOT WOOD (T., 1922, **121**, 2760—2765).

Crystal Structure of Titanium, Zirconium, Cerium, Thorium, and Osmium. ALBERT W. HULL (*Physical Rev.*, 1921, **18**, 88—89).—Titanium crystallises in the hexagonal system, holohedral class, with axial ratio 1·59±0·01. The side of the unit triangular prism is 2·97 Å. and its height 4·72 Å. The lattice is made up of two sets of these prisms, the atoms of one set being in the centre of the prisms of the other set. Zirconium has a similar structure, with axial ratio also 1·59. The side of the unit triangle is 3·23 Å. and its height 5·14 Å. Cerium has a similar structure with axial ratio 1·62. The side of the elementary triangle is 3·65 Å. and height 5·96 Å. A face-centred cubic form, with side of cube 5·12 Å., is also present, but may possibly be due to the presence of impurity. Thorium has a face-centred cubic lattice with side of cube 5·04 Å. Osmium crystallises in a face-centred cubic lattice with axial ratio 1·59. The side of the unit triangle is 2·714 Å. and its height 4·32 Å. A. A. E.

The Isotopes of Antimony. F. W. ASTON (*Nature*, 1922, **110**, 732).—The mass-spectrum of antimony, obtained by the use of antimony trimethyl, gives two lines at 121 and 123, respectively, the former being the more intense by 10—20%. The masses of these isotopes of antimony are most probably less than whole numbers by one to two parts per thousand. The results are in excellent agreement with the atomic weight (121·77) obtained by Willard and McAlpine (A., 1921, ii, 405) but not with the accepted figure (120·2). A. A. E.

The Alleged Variable Composition of Triple Chlorides containing Silver and Gold. HORACE L. WELLS (*Amer. J. Sci.*, 1922, [v], **4**, 476—482; cf. A., 1922, ii, 449, 514).—From Bayer's analyses of cæsium silver gold chloride (A., 1920, ii, 688) the conclusion is drawn that the triple salt, $Cs_2AgAuCl_6$, is a definite, invariable compound, and that Bayer analysed mixtures of this salt with $Cs_5Au_3Cl_{14}$, and $CsAuCl_4$. The rubidium salt, $Rb_6Ag_2Au_3Cl_{17}$, is also invariable. It is probable also that Suschnig (A., 1922, ii, 514) analysed mixtures in his investigation of the triple bromides of rubidium, silver, and gold. W. E. G.

Hydrolysis of Platinum Salts. II. Potassium Platinibromide. EBEN HENRY ARCHIBALD and WILLIAM A. GALE (T., 1922, **121**, 2849—2857).

Analytical Chemistry.

Bimetallic Electrode Systems in Electrometric Analysis. I. Systems comprising Two Dissimilar Metals. H. H. Willard and Florence Fenwick (*J. Amer. Chem. Soc.*, 1922, **44**, 2504—2515).—The constant half-cell of the usual electrometric titration apparatus may be replaced by a metal or certain alloys of metals of the platinum group, other than pure platinum or pure palladium, and by tungsten. The end-point obtained with such a bimetallic system differs in character from that given by an unimetallic electrode, but is situated in exactly the same position. Such a bimetallic electrode system has the advantage of being essentially simpler than the usual system and the end-point is much more distinct than with the ordinary electrode. J. F. S.

Bimetallic Electrode Systems in Electrometric Analysis. II. Theory of Bimetallic Systems: Systems comprising Two Similar Metals. H. H. Willard and Florence Fenwick (*J. Amer. Chem. Soc.*, 1922, **44**, 2516—2529).—In aqueous solutions of multivalent elements in which the concentration of either state of oxidation approaches the limiting value, the potential, unattackable electrode|solution, is determined by the magnitude of the solution pressure of gas absorbed by the electrode, and the end-point obtained in oxidimetric titrations with systems comprising two unattackable electrodes is given only by virtue of a difference in the solvent power of the two metals for gas. When the concentration of oxygen-ion, or hydrogen-ion, becomes vanishingly small, the osmotic pressure is too low for a saturation of the electrodes with the corresponding gas. The two elements receive the charge in accordance with the distribution law, and a difference in potential develops which is at its maximum with minimum concentration of the corresponding ion and falls rapidly as this ion-concentration rises to a value in excess of that required for the saturation of both electrodes. The bimetallic systems described (cf. preceding abstract) provide a type of electrode system essentially different from those previously used. A comparison of the relative values of the usual unimetallic and bimetallic systems may be based on the difference in the mechanism of the end-point in the two cases. The change in voltage with the former, which is a true oxidation-potential, is continuous throughout, and rises to a maximum at the end-point. With the latter practically all change is confined to within less than 0·5 c.c. of the completion of the titration. Although the actual magnitude of the break is normally less than with unimetallic combinations, it is, relative to the preceding rise, much greater, hence the sharpness of the end-point is correspondingly increased, insuring greater speed and accuracy. With the use of polarised bimetallic systems the break may be increased so much as to leave no possible

comparison favourable to the unimetallic system. It thus becomes possible to titrate solutions which offer too small potential differences between two possible states of oxidation for a good end-point with the usual apparatus. The polarising circuit may be made an integral part of the usual apparatus which requires no attention and presents no difficulties. The disadvantages of the new system lie in the greater localisation of the total potential change which makes it more difficult to anticipate the end-point. Enough warning is given, however, to make the danger of over-titration negligible after very little practice. J. F. S.

Estimation of Chlorine in Benzaldehyde. J. VOIGT (*Z. angew. Chem.*, 1922, **35**, 654—655).—An apparatus is described by means of which traces of chlorine in volatile organic compounds, particularly in synthetic benzaldehyde, can be accurately estimated. From 10—20 g. of benzaldehyde are weighed into a wickless lamp arranged in an air-bath which can be heated by bunsen burners. The exit of the lamp is connected with a pipette-shaped combustion tube through which oxygen is passed. Hydrogen is passed over the warmed benzaldehyde, and, mixing with the vapours, it carries them forward through a jet situated in the wide part of the combustion tube. The issuing gas is ignited in the oxygen by heating the tube externally, and it continues to burn quietly until all the benzaldehyde has been volatilised. The products of combustion pass over 2—3 g. of granulated anhydrous sodium carbonate packed in the narrow stem of the combustion tube and heated by a row of burners. The water is collected in a calcium chloride tower. About 7 g. of benzaldehyde can be burnt in an hour, and at the end of the combustion the soda is washed out of the tube by means of dilute nitric acid and titrated with standard silver nitrate. As little as 0·001% of chlorine can be estimated accurately by this method, and it is therefore necessary to apply a correction for the chlorine content of the hydrogen employed, as, although undetectable by ordinary methods, the amount which is always present may make an appreciable difference in the present case. Hydrogen in cylinders contains on the average 0·003 g. of chlorine per m^3. G. F. M.

Detection of Chlorides and Bromides in the Presence of Thiocyanates. G. SPACU (*Bul. Soc. Ştiinţe Cluj*, 1922, i, 302—305; from *Chem. Zentr.*, 1922, iv, 735).—Neutral solutions containing chlorides and bromides in the presence of thiocyanates are treated with a little pyridine and excess of 10% copper sulphate solution. The thiocyanate ion is quantitatively precipitated as copper pyridine thiocyanate, $[CuPy_2](CNS)_2$, and the filtrate may be tested in the ordinary way for chlorides and bromides.

G. W. R.

A Gasometric Method of Estimating the Halogen in Organic Compounds. ALEXANDER KILLEN MACBETH (*Chem. News*, 1922, **125**, 305—306).—Some organic halogen compounds in which the halogen possesses an induced electropositive nature

(cf. Henderson and Macbeth, T., 1922, **121**, 892) are reduced quantitatively by hydrazine, the volume of nitrogen evolved depending on the amount of halogen or halogen compound dealt with. A list of substances to which the method has been successfully applied is given. With some halogen-substituted malonic esters the reaction is not quantitative and in the case of certain di-substituted compounds only one halogen atom reacts, the other being unattacked in the cold. H. J. E.

Estimation of Fluorides. N. K. Smit (*Chem. Trade J.*, 1922, **71**, 325).—A simplification of Greeff's method (A., 1913, ii, 975). To 5 or 10 c.c. of the neutral fluoride solution are added 5 c.c. of 10% ammonium thiocyanate solution and 25 c.c. of alcohol, and the mixture titrated directly with alcoholic ferric chloride, standardised against potassium fluoride. The reaction between ferric chloride and fluorides can also be applied to the detection of the latter. A. A. E.

The Estimation of Oxygen in Steel. Georges Chaudron and Louis Blanc (*Compt. rend.*, 1922, **175**, 885—887).—In estimating oxygen in steel by heating the metal in a current of hydrogen and measuring the quantity of water formed, the addition of other metals to enable the estimation to be carried out at a lower temperature was not found to affect the result obtained. When dealing with molten mixtures of iron and oxide of manganese, or of iron and silicon dioxide, the method is inaccurate owing to incomplete reduction of the oxides and to the relatively small amount of water obtained which is of the same order as the corrections necessitated by the method. H. J. E.

Estimation of Sulphur in Iron and Steel. Ferdinand Nikolai (*Chem. Ztg.*, 1922, **46**, 1025—1026).—The iron or steel turnings or powder are treated with hydrobromic acid (d 1·48=47·4%) in an apparatus consisting of a small flask ground on to a tube, the first 12 cm. of which act as a reflux air condenser, and is then bent round and carried vertically downwards into a cylinder containing 2·5% sodium hydroxide solution. The mixture of iron and hydrobromic acid is gradually raised to its boiling point and the hydrogen sulphide liberated is absorbed in the sodium hydroxide solution, which, after adding 10 c.c. of potassium iodide solution and some starch, is titrated with $N/150$-iodine solution. The whole estimation requires twenty to twenty-five minutes, and very concordant results are obtained, which agree well with those obtained using Fresenius's method. The results obtained by the above method are higher than those obtained using either dilute or concentrated hydrochloric acid because the aqueous solution of hydrobromic acid which distils unchanged contains 47·4% HBr, whereas the corresponding hydrochloric acid solution only contains 20% HCl. H. C. R.

The Rapid Estimation of Sulphur Dioxide. R. Marcille (*Ann. Falsif.*, 1922, **15**, 398—401).—For the rapid and approximate

estimation of sulphur dioxide in wines, 10 c.c. of the wine are heated with 10 c.c. of a solution of 60 g. of sodium hydroxide per litre, in a wide-necked conical flask until the volume of the contents is reduced to one-half. The solution is cooled, diluted with 100—150 c.c. of water and enough dilute sulphuric acid added to neutralise the sodium hydroxide. Starch solution is added and the solution is titrated with iodine solution containing 4 g. or 8 g. per litre (1 c.c.=1 mg. or 2 mg. of sulphur dioxide). If the alcohol and aldehydes are not driven off by heating, the results may be 200 mg. per litre too low. The presence of more than 5 g. of dextrose per litre in the wine affects the results obtained and the sulphur dioxide must then be separated by distilling 10 c.c. of the wine acidified with 5 or 6 drops of syrupy phosphoric acid, the distillate being led into 10 c.c. of the sodium hydroxide solution, which is afterwards treated as in the direct method described above. The results obtained by this method agree well with those given by Haas's method, and the degree of accuracy is sufficient for all practical purposes. H. C. R.

New Process for the Volumetric Estimation of Ammonia and Carbamide Nitrogen by the Hypobromite Method. J. Tillmans and A. Krüger (*Z. angew. Chem.*, 1922, **35**, 686—687).—A simple glass apparatus is described for the estimation of ammonia or carbamide by the hypobromite method. It consists essentially of an upper cylindrical portion provided with a ground-glass stopper and a draw-off cock drawn out to a fine opening. The upper vessel fits with a ground-glass joint into a lower vessel and communication between them is established through a vertical tube extending nearly to the top of the upper chamber, which is charged with brine to a level of 3—4 cm. below the top of the vertical communication tube. When the draw-off cock is opened and the apparatus is otherwise closed, brine runs out until equilibrium is attained between the inside and outside pressures. The lower vessel being previously charged with hypobromite solution, the reaction is then started by rotating a boat containing the carbamide or ammonium salt on its axis so that its contents fall into the solution, and the nitrogen evolved causes the displacement of an equal volume of brine from the upper vessel through the draw-off cock. The boat is fixed to a horizontal axis which is ground to pass through, and fit into a tubulure in the side of the lower vessel, and the boat can be reversed by turning the projecting portion of the axis through 180°. The apparatus can be utilised for urine investigations by placing the urine in the lower vessel, and running in the hypobromite by means of a tap funnel through the vertical communication tube. G. F. M.

The Estimation of Aliphatic Nitrates in the Presence of certain Nitro-aromatic Compounds. Wilbert J. Huff and Richard D. Leitch (*J. Amer. Chem. Soc.*, 1922, **44**, 2643—2645).—Aliphatic nitrates may be estimated in the presence of certain aromatic nitro-compounds by reduction with ferrous sulphate in

excess, the unoxidised ferrous salt being titrated with standard permanganate solution. A Kjeldahl flask is fitted with a two-holed rubber cork carrying a pear-shaped dropping funnel and a tube bent twice at right angles and having its external orifice closed by a mercury seal. The air is expelled from the flask by boiling in it 25 c.c. of distilled water, and when the flame is removed the nitrate ester mixed with the aromatic compound and dissolved in glacial acetic acid is slowly run into the flask. Then a known volume of a standard solution of ferrous sulphate in dilute sulphuric acid is slowly added and this is followed by concentrated hydrochloric acid in volume equal to that of the liquid already in the flask. The reaction mixture is then evaporated to 10—15 c.c. and nearly neutralised with sodium carbonate, and when cool is diluted to 600 c.c. and after the addition of 2—3 g. of manganous sulphate is titrated with permanganate solution. Satisfactory results were obtained for mannitol hexanitrate, but those for glyceryl trinitrate were slightly low, probably owing to the partial vaporisation of the nitrate before it was completely hydrolysed. W. G.

New Reagent for the Detection of Nitrites in Water. GEORGES RODILLON (*J. Pharm. Chim.*, 1922, [vii], **26**, 376—379).—To the water to be examined, contained in a test-tube, 3—4 c.c. of a reagent, composed of a 6% solution of resorcinol in pure sulphuric acid, are added so as to form two layers. In presence of nitrites, a rose-coloured ring is formed at the junction of the two layers. An approximate estimation of nitrous acid can also be arrived at if desired by comparing the density of colour and the appearances of the ring and the aqueous and sulphuric acid layers with those obtained with standard sodium nitrite solutions. Thus the coloration of the ring with solutions containing in 1 litre 1 g. of sodium nitrate is brownish-black, fading away above and below to red; 0·1 g., brownish-red, similarly fading to red at the edges; 0·01 g., carmine, and 0·001 g., a very pale rose. The sulphuric acid layer ranges in colour with these concentrations from an intense amethyst-violet to the unchanged yellow of the original reagent.

G. F. M.

Volumetric Estimation of Phosphate in Solution. FRANK W. BURY (*J. Soc. Chem. Ind.*, 1922, **41**, 352T).—In the volumetric estimation of phosphate in solution by Rosin's method (A., 1911, ii, 768), the solution is kept neutral by means of zinc oxide. The neutralisation is very tedious, and copper carbonate was tried, but showed no advantage. The best results were obtained by neutralising with borax, the procedure being as follows. A measured quantity of phosphate solution is added to a measured excess of $N/10$-silver nitrate, and $N/10$-borax solution is run in until the liquid is neutral to litmus. The solution is then filtered, and the excess of silver nitrate estimated either by Volhard's method, or by adding a measured excess of $N/10$-potassium chloride and titrating back the excess with $N/10$-silver nitrate, using potassium chromate as indicator. G. F. M.

The Titration of Boric Acid in Presence of Phosphoric Acid. I. M. KOLTHOFF (*Chem. Weekblad*, 1922, **19**, 545—546; cf. A., 1922, ii, 867).—An answer to the criticisms of Deerns (A., 1922, ii, 867) on the citrate method put forward by the author.

S. I. L.

Estimation of the Radium Content of Low-grade Radium-Barium Salts. VICTOR F. HESS and ELIZABETH E. DAMON (*Physical Rev.*, 1922, **20**, 59—64; cf. *Trans. Amer. Electrochem. Soc.*, 1922, **41**).—The γ-ray method for the estimation of radium is inapplicable to salts containing much less than 10^{-4} g. of radium per g. if the customary apparatus is used, and the emanation method involves errors due to dilution and other causes, if the sample contains more than 10^{-7} g. of radium per g. For the examination of salts of intermediate radium content, the γ-ray method has been modified by the adoption of a shallow container with two curved sides, each concentric with the cylindrical string electrometer, and only a small fraction of the radius of curvature apart. Readings are taken with the container in position, full of the salt to be measured, first alone, and then with a small radium tube of known strength placed first immediately in front and then immediately behind the container. The ratio of the first reading to the mean of the other two gives that of the radium content of the salt under examination to the sum of the same and the standard to within 1%.

A. A. E.

Bismuth Sodium Thiosulphate; its Preparation and Use in the Estimation of Potassium. V. CUISINIER (*Bull. Soc. chim.*, 1922, [iv], **31**, 1064—1068).—Observations on the thiosulphates of bismuth and alkali metals have been made by Carnot (A., 1876, ii, 426), Hauser (A., 1903, ii, 487), Sanchez (A., 1912, ii, 562), and by Vanino and Mussgnug (A., 1920, ii, 44), but the substances have not been fully described and their use in the estimation of potassium salts has given inconsistent results. A salt of the approximate composition $Na_3Bi(S_2O_3)_3$ can be prepared, crystallising in yellow, prismatic plates rapidly turning brown on exposure to air. On attempting to carry out estimations of potassium by precipitation as potassium bismuth thiosulphate and subsequent treatment of the precipitate with iodine, it was found that the results obtained were too high. Further, the amount of precipitate obtained appears to be influenced by the concentration of the reacting solutions; the iodine value is not proportional to the potassium content of the solution investigated, and the volume of the alcohol used as precipitant also affects the result obtained. [Cf. *J.S.C.I.*, 1922, 981A.]

H. J. E.

A Photochemical Test for Silver in Thin Sections of Ores. G. SILBERSTEIN and E. WIESS (*Z. anorg. Chem.*, 1922, **124**, 355—356).—On placing the section in a saturated solution of an iodide for five minutes, the silver is covered with a thin film of silver iodide, which, under the microscope, showed the characteristic reaction to light. The authors propose investigating the practical

limits of this test, and also the light reaction of silver sulphide, with the object of applying it to test for sulphur in metals by shaking them with a solution of a silver salt. W. T.

Contradictions and Errors in Analytical Chemistry. III. The Separation of Zinc from Magnesium, Calcium, and Aluminium by Precipitation of the Phosphates. IV. The Conversion of Alkali Sulphates into Chlorides. FRIEDRICH L. HAHN [with (III) J. DORNAUF and (IV) R. OTTO] (*Ber.*, 1922, **55**, [*B*], 3434—3436; cf. A., 1922, ii, 873).—III. The separation of magnesium, calcium, and aluminium from zinc can be effected according to Voigt (A., 1910, ii, 74) by precipitation with phosphate in ammonical solution containing ammonium salts whereby only the zinc remains dissolved. This method of separation has great advantages when only small quantities of foreign metals are present, but the subsequent operation of precipitating the zinc as the zinc ammonium phosphate cannot be effected quantitatively by simply boiling the solution until the excess of ammonia is expelled. Accurate results are obtained if the filtrate containing the zinc is treated with hydrochloric acid until just acid to methyl-red and subsequently with an excess of phosphate. If the solution is rich in ammonium salts, it is preferable to expel the bulk of the ammonia before addition of the acid.

IV. Potassium cannot be separated from sodium as the perchlorate or chloroplatinate if the metals are present as sulphates. The usual procedure of precipitating the latter with barium chloride, removal of excess of barium with ammonium carbonate, and subsequent volatilisation of the excess of ammonium salts, is inaccurate, since barium sulphate always carries down alkali sulphate. This difficulty can be overcome by precipitating the barium sulphate in extreme dilution. For this purpose, moderately dilute solutions of sulphate and barium chloride are added simultaneously and at approximately equivalent rates to a small quantity of boiling hydrochloric acid. Pure barium sulphate is thereby precipitated in well-formed, coarse crystals which are readily filtered and washed. The presence of varying amounts of alkali chloride and even of nitrate in the sulphate solution is without influence. If ferric iron is present, ammoniacal barium chloride solution must be used and the solution be acidified after the precipitation. H. W.

The Carrying-down of Zinc by Copper Sulphide. I. M. KOLTHOFF and J. C. VAN DIJK (*Pharm. Weekblad*, 1922, **59**, 1351—1360).—The fact that zinc sulphide is almost always precipitated to some extent with copper sulphide from solutions of the two metals is not due to adsorption, since zinc sulphide is only with difficulty soluble in acids of low concentration. The precipitation of zinc from acid solutions by hydrogen sulphide depends on time and temperature, as well as on the concentration of zinc-, hydrogen-, and sulphide-ions, and is accelerated by presence of copper sulphide.

In the quantitative separation of copper and zinc by hydrogen

sulphide, the time must be as short as possible. If sulphuric or hydrochloric acid is used, the acidity must be at least $0{\cdot}5N$; with the former, room temperature is best; with the latter, the gas should be led in at the boiling point. S. I. L.

Some Applications of Sodium Peroxide in Analytical Chemistry. W. M. STERNBERG (*Science*, 1920, **52**, 162).—The decomposition of lead and zinc ores by fusion in an iron crucible with at least six to eight parts of sodium peroxide is rapid and complete. In the case of lead ores, the aqueous solution of the fused mass, after treatment with 1·4 parts of oxalic acid to reduce the lead dioxide, is acidified with sulphuric acid, boiled, cooled, and the lead sulphate collected and washed with 5% sulphuric acid. It is then dissolved in a solution of ammonium chloride or of ammonium chloride and sodium acetate, and titrated with ammonium molybdate. In the case of zinc ores, the fused mass is dissolved in ammoniacal ammonium chloride solution, the solution boiled, filtered, and washed with hot ammonium chloride solution, acidified with hydrochloric acid, boiled, and titrated with potassium ferrocyanide after the addition of hydrogen sulphide. It is necessary that the solutions should be standardised against a standard ore treated by the same method. A. A. E.

Gravimetric Analysis. XXVI. Estimation of Lead. L. W. WINKLER (*Z. angew. Chem.*, 1922, **35**, 662—663).—For the gravimetric estimation of lead in neutral solution, 100 c.c. of lead nitrate or lead chloride solution containing from 0·60 to 0·01 g. of lead is acidified with 1 c.c. of normal nitric acid solution and boiled. Ten c.c. of 10% ammonium sulphate solution are slowly run in, and the whole is allowed to remain, then filtered. The precipitate is washed with 50 c.c. of a cold saturated solution of lead sulphate, and the edge of the filter washed with 1—2 c.c. of dilute alcohol. The precipitate is dried for two hours at 130°. Modifications of the procedure necessitated by the presence of nitric or hydrochloric acid, and salts of potassium or other metals, are discussed and details are given of the method of estimation of lead in crude lead, minium, lead chromate, and lead salts of organic acids. J. S. G. T.

A New Sensitive Reaction for Copper, Thiocyanate, and Pyridine. G. SPACU (*Bull. Soc. Ştiinţe Cluj*, 1922, **1**, 284—291; from *Chem. Zentr.*, 1922, iv, 737).—The reaction consists in the formation of a light green precipitate when a neutral solution of a copper salt is treated with a neutral thiocyanate and a few drops of pyridine. The precipitate has the composition $[CuPy_2](CNS)_2$ and is almost completely insoluble in water. The reagent must be neutral and excess of pyridine must be avoided. The pyridine should be added before the thiocyanate. One part in 300,000—800,000 of copper can be detected according to the conditions of experiment. For pyridine, the sensitiveness is one part in 2000 and for thiocyanate one in 50,000. G. W. R.

The Hindering of the Precipitation of Copper Sulphide by the Presence of Sodium Chloride. WILHELM BILTZ (*Ber.*, 1922, **55**, [*B*], 3393).—In a recent communication, Dede and Bonin (A., 1922, ii, 766) have shown that lead and cadmium sulphides are only incompletely precipitated in hydrochloric acid solution in the presence of relatively large quantities of the chlorides of the alkali or alkaline-earth metals. Similar observations have been recorded in the case of copper (cf. Biltz and Marcus, A., 1909, ii, 1011). Precipitation of copper sulphide is, however, quantitative in a 5% solution of sodium chloride. Magnesium chloride or carnallite does not appear to have an inhibiting action. H. W.

A New Microchemical Reaction for the Estimation of Copper. G. SPACU (*Bull. Soc. Ştiinţe Cluj*, 1922, **1**, 296—301; from *Chem. Zentr.*, 1922, iv, 737—738).—After precipitation of copper as copper pyridine thiocyanate, $CuPy_2(CNS)_2$ (see this vol., ii, 40), the precipitate is separated in an appropriate apparatus (Rothe's shaking funnel) by successive extraction with chloroform. The precipitate is then weighed, after removal of the chloroform in a vacuum desiccator. Alternatively, the precipitate may be ignited, and the copper estimated as cupric sulphide or cupric oxide. G. W. R.

Volumetric Estimation of Copper, and its application to the Estimation of Reducing Sugars. ED. LASAUSSE (*J. Pharm. Chim.*, 1922, [vii], **26**, 401—406).—The precipitated cuprous oxide formed by the reducing action of the sugar on a cupro-tartrate solution is collected on a Gooch crucible and dissolved by means of 2—3 c.c. of nitric acid. The filter is finally washed with water, the total volume of filtrate and washings being kept below 25—30 c.c. The nitrous acid present is then eliminated by adding 2% permanganate solution drop by drop to the boiling liquid until the pink coloration just persists, and the latter is reduced by the addition of a few drops of alcohol. After boiling for a minute longer, the precipitated oxides of manganese are filtered off, the filtrate is made up to 100 c.c., and the copper is estimated iodometrically in the usual way after the addition of an excess of sodium acetate to displace free mineral acid. In order to obtain the best results in the estimation of reducing sugars, the procedure of Quisumbing and Thomas should be followed (A., 1922, ii, 92) as a granular cuprous oxide is thereby obtained, which can readily be collected and washed. The amount of dextrose is given by the formula $0{\cdot}474x+0{\cdot}000115x^2$, and of invert-sugar by $0{\cdot}504x+0{\cdot}000087x^2$, where x is the weight of copper reduced. G. F. M.

Iodometric Estimation of Copper in Bronze and Brass. G. BATTA and G. LATHIERS (*Bull. Soc. chim. Belg.*, 1922, **31**, 297—302).—The application of the iodometric method of copper estimation to bronze and brass gives results which are of sufficient accuracy for many purposes. It is rapid and useful when electrolytic methods cannot be employed. H. J. E.

Rapid Electrolytic Estimation of Mercury. A. DE MEEÛS (*Bull. Soc. chim. Belg.*, 1922, **31**, 302—323; cf. Böttger, A., 1921, ii, 351).—A study of the factors which are said to cause inaccuracies in the electrolytic estimation of mercury. Good results were obtained with a platinum cathode, but gold was found to be more suitable for the purpose as the mercury deposit is more adherent and so permits of the use of alcohol and ether for washing; in the case of other metals this should be done with water only as the more rapid method occasions loss. Experiments carried out with mercuric salts in presence of substances which form complexes give similar results with gold and platinum cathodes, but the method is more satisfactory when simple acid electrolytes are used as solvents. The method is applicable to mercurous salts, which are oxidised before electrolysis. H. J. E.

Constancy of the Titer of Permanganate Solutions, and Different Methods of Standardisation. O. HACKL (*Chem. Ztg.*, 1922, **46**, 1065).—N/10-solutions of potassium permanganate made from the freshly prepared pure salt remained permanent, if stored in a dark place for one year, whereas solutions made from a ten-year old preparation altered considerably in the course of a few months. Tests showed that the most satisfactory compound for use in standardisation of permanganate solutions is sodium oxalate. The composition of oxalic acid crystals and ferrous ammonium sulphate was found to vary within narrow limits, but these are sufficient to lead to discordant results in the titration. A. R. P.

The Electrometric Estimation of Iron and Vanadium when present together. ERICH MÜLLER and HANS JUST (*Z. anorg. Chem.*, 1922, **125**, 155—166).—Ferrous salts and vanadium salts can be accurately estimated electrometrically with permanganate. Ferrous salts are more vigorous reducing agents than the salts of quadrivalent vanadium, and the authors find that they can be estimated when together in the same way. To the mixture, a decinormal solution of potassium permanganate is gradually added until there is a sudden change in the *E.M.F.* This indicates the end-point for the ferrous salt; the titration is then continued until a second sudden change occurs which represents the end-point for the vanadium salt. The latter titration is best carried out at about 70° as the reaction is very slow at the ordinary temperature. W. T.

Electrometric Standardising of Titanous Solutions. W. S. HENDRIXSON and L. M. VERBECK (*J. Amer. Chem. Soc.*, 1922, **44**, 2382—2386).—A slightly acid solution of titanous sulphate may be used to standardise solutions of potassium permanganate or potassium dichromate. The method consists in adding the titanous solution to the permanganate or dichromate solution and measuring the *E.M.F.* of the solution toward a platinum electrode against a calomel electrode. The *E.M.F.* changes very rapidly at the end-point, which is therefore made very precise; in the case of

dichromate, the change in *E.M.F.* on adding a slight excess of titanous ion to a slight excess of dichromate is about 0·6 volt, whilst in the case of permanganate the change in *E.M.F.* is about 0·9 volt. This difference makes it possible to estimate two substances of quite different oxidising power in the same solution. The authors have investigated the estimation of titanous and ferrous ions by means of permanganate or dichromate, of ferric-iron and dichromate or permanganate by means of a titanous solution, and have found that the method is trustworthy. J. F. S.

New Method for the Gravimetric Estimation of Germanium. John Hughes Müller (*J. Amer. Chem. Soc.*, 1922, **44**, 2493—2498).—A new method of estimating germanium is described which is based on the precipitation of this metal as magnesium orthogermanate and weighing the dried and ignited precipitate. Magnesium orthogermanate is a snow-white, infusible substance, which is prepared by the action of magnesium sulphate, ammonium sulphate, and ammonium hydroxide on a solution of germanic acid. No precipitate is formed until the ammonium hydroxide has been added, and the reagents are added in the order named. Magnesium orthogermanate is amorphous and is very soluble in dilute solutions of acids, but after ignition it is only slowly dissolved by concentrated acids. It dissolves in water to the extent of 0·000016 g. per c.c. at 26°. In a mixture of two volumes of ammonia (0·880) and three volumes of water the solubility is 0·00002 g. per c.c., whilst in an ammoniacal solution of 10% ammonium sulphate the solubility is 0·00013 g. per c.c. at 26°. The estimation of germanium is effected by adding an excess of 2*N*-magnesium sulphate to the cold solution of germanic acid; this is followed by at least an equal volume of 2*N*-ammonium sulphate, and then ammonium hydroxide (0·880) is added in amounts varying from 15 c.c. to 20 c.c. for each 100 c.c. of solution and the mixture stirred vigorously, raised to the boiling point for a few minutes, and kept for ten to twelve hours before filtering. The precipitate is filtered, washed with a mixture of 90 c.c. of water and 10 c.c. of ammonia, dried, and ignited with free access of air. The results of the analyses are excellent. J. F. S.

Analysis of Mixtures of Hydrogen with Paraffin Hydrocarbons. J. G. King (*Fuel*, 1922, **1**, 103—106).—The estimation of hydrogen in admixture with paraffin hydrocarbons is effected by fractional combustion over copper oxide at 280°, in an apparatus which is a modification of that of Jäger (*J. Gasbeleuchtung*, 1898, **41**, 764). Carbon monoxide and hydrogen are thereby consumed, whereas the paraffins remain unchanged. Chemical Abstracts.

Identification of Methyl Alcohol in Liquids containing Ethyl Alcohol. I. M. Kolthoff (*Pharm. Weekblad*, 1922, **59**, 1268—1274).—The method of Denigès (A., 1910, ii, 461), namely, oxidation with permanganate in presence of acid, removal of excess with oxalic acid, and testing for formaldehyde with Schiff's reagent, will detect 0·05% of methyl alcohol in ethyl alcohol. The reagent

is best prepared as suggested by Elvove (A., 1917, ii, 341), and if kept in stoppered bottles is stable for long periods. The use of phosphoric acid in place of sulphuric acid, as recommended by Chapin (A., 1921, ii, 598), is found advantageous.

The method can be applied to the examination of tinctures and medicinal preparations containing alcohol, without preliminary distillation. The reagent will also detect formaldehyde in milk.

S. I. L.

Colour Reaction for Phenols based on the Use of Selenious Acid. VICTOR E. LEVINE (*Science*, 1920, **52**, 207).—A reaction of great sensitivity and wide applicability consists in the fact that phenols in contact with a solution of selenium dioxide (0·5%) or sodium selenite (0·75%) in concentrated sulphuric acid give rise to characteristic green or blue colorations. On heating, or on the addition of water, the colour changes to brown or red. It is considered that the phenol causes the liberation of selenium, which then dissolves with a green colour in concentrated sulphuric acid to form selenosulphur trioxide. A list is given of phenolic substances to which the test has been applied. A. A. E.

The Action of Proteins on the Phenol Reagent of Folin and Denis. VICTOR E. LEVINE (*Science*, 1920, **52**, 612—613).—The phosphotungstic-phosphomolybdic reagent of Folin and Denis (A., 1912, ii, 1011) is not specific for the phenolic group. The colour reaction is given by proteins, and in fact by a large number of inorganic and organic substances. The reagent appears to be affected by substances possessing more or less reducing properties.

A. A. E.

Test for Sugar in Urine. VICTOR E. LEVINE (*Science*, 1920, **52**, 391).—One to 2 c.c. of urine are heated for several minutes with 5 c.c. of a 2% solution of sodium tellurite in 10% sodium carbonate. Reduction to tellurium takes place in the presence of carbohydrates possessing a free carbonyl group. With small amounts of sugar, the tellurium forms a colloidal solution, which has a characteristic brown colour in transmitted light and is greyish-black in reflected light; larger amounts yield a greyish-black precipitate. A. A. E.

The Partition Coefficients, and the Estimation by Extraction of Organic Acids. JOH. PINNOW (*Z. Unters. Nahr. Genussm.*, 1922, **44**, 204—209).—Acetic and formic acids form double molecules in ethereal solution, and the irregularities observed in the partition coefficient of the latter acid may be ascribed to this cause. Assuming that no double molecules occur in the aqueous solutions, the dissociation coefficients of the double molecules have the following values at 15°: acetic acid, 1·776; formic acid, 4·77. The partition coefficients (water/ether) of the simple molecules at 15° are: acetic acid, 2·21; formic acid, 2·38. At 26·3°: formic acid, 2·79. Sugar has no effect on the extraction of succinic acid from its aqueous solution. H. C. R.

General and Physical Chemistry.

The Secondary Spectrum of Hydrogen. A. C. MENZIES (*Nature*, 1922, **110**, 876).—Silberstein's solution of the three-substance problem, applied by him to the case of neutral helium, has been modified so as to apply to hydrogen, and the value of N has been corrected so as to take account of the fact that with two electrons instead of one, the correction to the mass of the electron for the finite mass of the nucleus is no longer the same. Frequencies have been calculated from the formula $\nu=N_{\infty}(1/n_1^2+1/n_2^2-1/m_1^2-1/m_2^2)$ where $N_{\infty}=N_H(1+m/M)$. Forty-seven lines in the secondary spectrum of hydrogen were found to agree with the calculated values within an absolute error of one unit of frequency. The frequencies are regarded as a kind of "summation tone," being the sums of a Balmer or a Paschen frequency and a frequency in the ultra-red. In several cases, a physical similarity of behaviour was common to "series" of the lines grouped according to values of m and n. A. A. E.

Spectrum of Active Nitrogen as Affected by Admixture of the Inert Gases, with a Note on the Origin of the Cyanogen Spectrum. LORD RAYLEIGH (*Proc. Roy. Soc.*, 1923, [*A*], **102**, 453—459).—The afterglow accompanying the reversion of active nitrogen to ordinary nitrogen was shown by Fowler and Strutt (A., 1911, ii, 678) to be composed of a selection of the first positive bands of nitrogen. The addition of inert gases to the nitrogen produces considerable changes in the intensities of these bands. The maxima of the three groups of bands, green, yellow, and red, are shifted towards the red. The addition of helium, neon, or argon makes the red group as a whole, more intense at the expense of the others. The movement of the bands is proportional to the concentration of the inert gases present. Evidence is adduced for the belief that the red aurora line, λ 6320, is due to the presence of nitrogen and helium in the upper atmosphere. It is not yet determined whether the effects on the after-glow spectrum are produced in the electric discharge or in the process of the after-glow.

The influence of carbon in developing the cyanogen bands is discussed. W. E. G.

The Carbon Arc Spectrum in the Extreme Ultra-violet. F. SIMEON (*Proc. Roy. Soc.*, 1923, [*A*], **102**, 484—496).—Measurements are made of the ultra-violet lines of the carbon arc spectrum by means of a vacuum grating spectrograph. Colour sensitised Schumann plates were used both for the extreme ultra-violet as well as for the ordinary violet region. A table is given of the wavelengths and intensities of the lines observed, and comparison made with the values of other workers. Some of the lines photographed in the Lyman region have not been mentioned by any previous

worker, and some of the lines in the higher orders of spectrum have been shown to consist of close groups of lines. The line 599·0 attributed by Lyman to helium is due to carbon present as an impurity in the helium. The lines in the Lyman region at 1194, 945, 858, 687, 651, 640, 599, and 595 have not been previously observed in the arc spectrum of carbon, but these lines correspond with prominent lines in the "hot spark" spectra of Millikan. Groups at 1657, 1329, 1260, 1194, 1036, and 651 have been resolved into a number of lines. W. E. G.

The Spectrum of Neutral Helium. LUDWIK SILBERSTEIN (*Nature*, 1923, **111**, 46—47).—In reply to Raman's criticisms (A., 1922, ii, 803), it is shown mathematically that the probability that the forty-five coincidences previously described are fortuitous is less than $1 \cdot 7 \times 10^{-13}$; it is further claimed that the use of the value 109723 for the Rydberg constant in the formula applied to the case of the neutral helium atom (with two electrons) is justifiable. It is now found that the whole diffuse series of singlets, $1P-mD$, is represented by the formula $\nu=4N(18 \, . \, 2n/20 \, . \, 4) \equiv N(9 \, . \, n/10 \, . \, 2)$, two final and one initial quantum numbers being fixed. The possibility of reducing $4N$ to N, based on the fact that all numbers are even, is mentioned but not discussed; physically interpreted, it would mean that the helium nucleus attracts each of its electrons with only one-half of its total charge, as if its lines of force formed two bundles, each entirely engaged with one of the two trabants. A. A. E.

Relative Visibility of Spectra when an Electric Discharge is Passed Through the Vapours of Alkali Amalgams. F. H. NEWMAN (*Phil. Mag.*, 1923, [vi], **45**, 181—189).—The relative intensities of the spectra of the alkali metals and mercury have been examined by placing alkali amalgams in an electric discharge tube. For sodium and mercury the spectrum of the former was prominent at all temperatures, but below 100° the mercury spectrum was the brighter. At 200°, the mercury lines are almost entirely masked. At this temperature, a very brilliant yellow radiation is emitted, which forms a very convenient source of the sodium *D*-lines. The ionising potentials of sodium (5·13 volts) and mercury (10·2 volts) and the partial pressures of their vapours are the two main factors operative in determining the intensity of the spectra. At low vapour pressures, the atoms of both sodium and mercury will be so far apart that the electrons attain the necessary energy to ionise the mercury atoms before inelastic collision occurs. Under these conditions, approximately equal numbers of mercury and sodium atoms will be ionised. As the temperature rises, the density of the vapour increases, and the electrons attain less frequently the speeds corresponding with 10·2 volts, so that although the number of mercury atoms will be far more numerous that those of sodium, the actual number of the former ionised will be very small. Thus at 200° the mercury lines are suppressed. Except in the case of potassium, where the

lines are faint at all temperatures, the other alkali amalgams show similar phenomena. W. E. G.

The Excitation of the Mercury Spectrum. The Influence of Helium. GEORGES DÉJARDIN (*Compt. rend.*, 1922, **175**, 952—955).—An examination of the radiations emitted by mercury vapour traversed by electrons of different velocities showed that when the speed of the electrons is slightly greater than the critical ionisation velocity a large number of the arc spectrum lines are obtained, these being due to collisions between electrons and mercury atoms. When the conditions are such that the electron charge is neutralised, a luminous region appears near the electrodes the spectrum of which also exhibits the characteristics of that of the mercury arc. The author concludes that the emission spectrum appears to depend on the ionisation of the atom and notes the conditions under which certain of the lines become visible. In the presence of helium and with a potential greater than 20·4 volts, considerable modifications of the mercury spectra take place. Details of the variations in intensity and the appearance of new lines are given, the action of helium being apparently selective on certain lines as in the case of cadmium (cf. Collie and Watson, A., 1918, ii, 383). H. J. E.

Spectroanalytical Investigation of a New Element in the Terbium Group and the Arc Spectrum of Terbium. JOSEF MARIA EDER (*Sitzungsber. Akad. Wiss. Wien, Math.-naturwiss. Klass.*, 1922, [ii*a*], **131**, 199—298; cf. *ibid.*, 1920, **129**, 422).—The determination of the spectra of a number of terbium, dysprosium, and gadolinium fractions has led to the discovery of a new element giving a well-defined and characteristic line spectrum. This element, which was present in a fraction between terbium and dysprosium, is named *Welsium*. The lines of the new element are weakened in the spectra of the fractions rich in terbium, and are practically absent in the spectra of the dysprosium fractions. In agreement with the observations of Eberhard, no evidence has been found for a new element in the fractions between terbium and gadolinium.

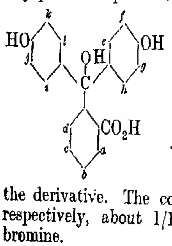
Many thousands of lines of the terbium spectrum have been measured between λ 7257 and 2400 Å., and compared with the measurements of Urbain, Eberhard, and Auer. W. E. G.

The Line Spectrum of Vanadium in Fused Salts. A. DE GRAMONT (*Compt. rend.*, 1922, **175**, 1129—1133; cf. A., 1921, ii, 73).—A solution of vanadium pentoxide in fused sodium carbonate was used in order to ascertain the limiting quantity of vanadium capable of spectroscopic detection. The results are shown in two tables which give, for visual and photographic observation, respectively, the smallest quantity corresponding with each line in the spectrum. Non-conducting materials which contain vanadium give good spark spectra which are in accordance with the author's observations. H. J. E.

Absorption of Light by Chlorine. H. VON HALBAN and K. SIEDENTOPF (*Z. physikal. Chem.*, 1922, **103**, 71—90).—The absorption of light by chlorine between 254 $\mu\mu$ and 643 $\mu\mu$ has been determined for nineteen wave-lengths, using lines of mercury, zinc, and cadmium, and between 383 $\mu\mu$ and 451 μ, using a Nitra-lamp for twelve wave-lengths. The method of observation was the previously described photoelectric two-cell arrangement (A., 1922, ii, 332). The results show that within the pressure range investigated (760 mm. and downwards) Beer's law is true. The absorption curve shows a maximum in the ultra-violet at about 334 $\mu\mu$ and a minimum in the yellow. From yellow to red, the absorption again increases, and reaches a maximum which probably lies between 614 $\mu\mu$ and 643 $\mu\mu$. No difference could be observed between the absorption of dry and moist chlorine. J. F. S.

The Ultra-violet Absorption Spectra of Toluene and the Xylenes. F. W. KLINGSTEDT (*Compt. rend.*, 1922, **175**, 1065—1067).—The ultra-violet absorption of hexane solutions of toluene and of the xylenes was measured, and details of the position and form of the bands are given, together with a diagrammatic representation. Toluene exhibits sixteen bands, as compared with eight for benzene in the same region; the intensity of absorption is a little greater than that of benzene. The bands are divided into four groups, in each of which intensity decreases with wave-length. Three large bands are observed with *o*-xylene and five with *m*-xylene, whilst in the case of *p*-xylene the absorption coefficient is about four times as great, and the spectrum contains twelve bands arranged in three groups. H. J. E.

Colour and Chemical Constitution. XV. A Systematic Study of Fluorescein and Resorcin-benzein. JAMES MOIR (*Trans. Roy. Soc. S. Africa*, 1922, **10**, 159—164; cf. A., 1922, ii, 333).—The quantitative study of the colour of compounds of the phenolphthalein type has been continued. The results previously recorded for the bromophenolphthaleins (A., 1921, ii, 365) are restated in another form. The different positions open to substitution in the phenolphthalein molecule are lettered as shown. The colour modification due to the introduction of bromine into any particular position can be expressed by a factor, the "dicyclic colour factor," by which the characteristic wave-length of phenolphthalein must be multiplied to give that of the derivative. These factors, for the respective positions, are: *a* and *d*, 1·018; *b*, 1·002; *c*, *f*, and *g*, 1·0145; *e* and *h*, 1·0270; *i* and *l*, 1·0235; *j* and *k*, 1·0125. If two or more positions are substituted, all the corresponding factors must be used in calculating the colour of the derivative. The colour factors for chlorine and iodine are, respectively, about 1/1500 smaller and greater than those for bromine.



Similar factors have been worked out for various substituents

in fluorescein, $\lambda=493.5$. For bromine, the factors for the different positions are: *a* and *d*, 1·0162; *b*, 1·0000; *c*, 1·0091; *f* and *k*, 1·0122; *g* and *j*, 1·0157. The factors for nitro-derivatives are very similar to those for bromo-derivatives, the methyl factors are smaller and the methoxy-factors smaller still, the largest being 1·006. The hydroxy-factors are smallest of all, and in sodium hydroxide solution the hydroxy-derivatives have their absorption bands in the same position as fluorescein itself. Gallein and hydroxyquinolphthalein are exceptions to this rule.

Resorcin-benzein, which is fluorescein without the carboxyl group, is practically identical with fluorescein in alkaline solution; the absorption band is at λ 492. A few derivatives which have been examined show that the colour factors for the *f*, *g*, *j*, and *k* positions are the same as those of phenolphthalein. In the phenyl ring, the effect diminishes in the order *d*, *c*, *b*, but is still positive for *b*, although in fluorescein it appears to be nil for this position.

E. H. R.

Ultra-violet Absorption Spectra of Alkaloids of the *iso*-Quinoline Group. Papaverine and its Hydrochloride. PIERRE STEINER (*Compt. rend.*, 1922, **175**, 1146—1149).—A comparison of the absorption spectra of papaverine with those of *iso*-quinoline and veratrole, the substances of which the alkaloid is constituted, shows that it is similar to that of *iso*quinoline but simpler. The simplification appears to be due to the veratrole group, which also determines a displacement towards the red and an increase in absorption. The spectrum of the alkaloid is similar in ethereal and in alcoholic solutions; in the latter, a shifting of four bands towards the red is observed. The combination with hydrochloric acid causes a fusion of three absorption bands exhibited by the alkaloid together with a general displacement towards red and increase in absorption. The spectrographic method applied to the detection of papaverine permits of the recognition of 0·03 mg. in 2 c.c. of solution. H. J. E.

Kinetics of Photochemical Reactions. RUDOLF WEGSCHEIDER (*Z. physikal. Chem.*, 1922, **103**, 273—307).—A theoretical paper in which the laws of photochemical kinetics are developed on the basis of the assumptions made for ordinary chemical reactions. Van't Hoff's law of the proportionality between the amount of chemical change and the amount of light absorbed holds when the conversion of only one molecular species into the reactive condition by the light determines the velocity of the reaction; that is, the spontaneous return of the active molecules into the inactive form may be neglected and all other partial reactions of the total change take place instantaneously. It is to be expected that the law will not hold for the total reaction if the photosensitive molecular species is in excess of the other molecular species participating in the reaction; this is particularly the case in changes which have proceeded nearly to completion. Einstein's equivalent law determines, for energy storing reactions, the velocity constant of van't Hoff's formula, or gives at least the upper limit

for the total reaction. An upper limit of the velocity, only, can be obtained by thermodynamical methods for energy storing reactions. Velocity equations have been integrated on the assumption of van't Hoff's law and a homogeneous parallel beam of light, for a system which is continuously agitated and in which the light is absorbed either by a molecular species which is being destroyed by the reaction or by a sensitiser, which may have a constant concentration or may be produced by the reaction. A number of other possibilities and conditions in the reactions are also theoretically considered. It is also shown that when in a given reaction two photosensitive molecular species are present it is not likely that the velocity of reaction will be proportional to the product of the two quantities of absorbed light, but rather is a proportionality between the velocity and the second or higher power of the light intensity to be expected if a slower subsequent reaction requires the participation of several activated molecules.

J. F. S.

Photochemical Decomposition of Hydrogen Peroxide. CHR. WINTHER (*Danske Vid. Selsk. Mat.-phys. Medd.*, 1920, **2**, 3—18; from *Chem. Zentr.*, 1922, iii, 981).—Hydrogen peroxide in the presence of potassium ferrocyanide in dilute solution is decomposed on illumination with ultra-violet light. The reaction proceeds at first slowly, then more rapidly, and finally slows down. This decomposition of hydrogen peroxide is attributed to the formation of a catalyst by the influence of light on potassium ferrocyanide solution. The production of the catalyst increases with the time of illumination and reaches a maximum which depends on the amount of energy of the ultra-violet radiation and also, to some extent, on the concentration of hydrogen peroxide.

G. W. R.

Spacial Progression of Photochemical Reactions in Jellies. A. BENRATH and K. SCHAFFGANZ (*Z. physikal. Chem.*, 1922, **103**, 139—154).—The photochemical actions between ferric chloride and tartaric acid, silver bromide, and chlorine water have been examined when the reacting substances were uniformly distributed through various jellies such as silicic acid, starch, egg-albumin, gelatin, and various animal membranes. It is shown that the progression of photochemical reactions in jellies proceeds according to Lambert's law if the jelly absorbs the active rays, but if the jelly does not absorb these rays then the progression of the reaction is proportional to the time. From the experiments on the decomposition of chlorine water it is shown that the photosensitive component is the hypochlorite-ion. Organic jellies are shown to possess a considerable transparency for ultra-violet light, whilst animal membranes allow only a very little of the ultra-violet light to pass through them.

J. F. S.

Photocatalysis. III. The Photosynthesis of Naturally Occurring Nitrogen Compounds from Carbon Dioxide and Ammonia. EDWARD CHARLES CYRIL BALY, ISIDOR MORRIS HEILBRON, and HAROLD JACOB STERN (T., 1923, **123**, 185—197).

Spectrophotoelectrical Sensitivity of Argentite (Ag_2S). W. W. COBLENTZ (*Bull. Bur. Standards*, 1922, **18**, 265—280; *Sci. Paper*, No. 446).—A study of the effect of crystal structure on the photoelectrical sensitivity of silver sulphide. A comparison is made between the results for acanthite (A., 1920, ii, 212), and those now obtained for argentite. Appreciable changes in the electrical resistance of argentite and acanthite occur when these substances are exposed to wave-lengths of light extending from 0·3—2 μ, maxima being obtained at 1·35 μ and 0·41 μ. Argentite reacts slightly to radiation of wave-lengths 0·5 to 1·1 μ, whereas acanthite shows a strong photoelectrical sensitivity in this region. The maximum at 1·35 μ is symmetrical in the former, and unsymmetrical in the latter case. The maximum shifts to short wave-lengths at low temperatures. The photoelectrical reaction of argentite differs from that of acanthite in being free from an induced photonegative polarisation. On increasing the intensity of the radiation, in both cases, a more rapid change is produced in the long wave-lengths than in the short wave-lengths, and the maximum photoelectrical sensitivity is shifted toward the long wave-lengths.

Mechanical working of the crystals of acanthite and argentite lowers the photoelectrical sensitivity. The worked specimens of these minerals give practically identical infra-red maxima at low temperatures, the effect of temperature being less than in the naturally occurring crystals. Thus, apart from the effect of crystal structure, silver sulphide has a characteristic photoelectrical response spectrum. Crystal structure has, however, a marked effect upon photoelectrical sensitivity. W. E. G.

The Excitation of Characteristic *X*-Rays from Light Elements. J. C. MCLENNAN and (Miss) M. L. CLARK (*Proc. Roy. Soc.*, 1923, [*A*], **102**, 389—410).—Following the method of Hughes (A., 1922, ii, 184), the critical absorption wave-lengths of the *K*- and *L*-series were determined for the elements boron, glucinum, and lithium, and the critical absorption wave-lengths of the *L*-series for carbon. The following values were obtained: carbon, *L*-series, λ=166·7 Å.; boron, *K*-series, λ=83·6 Å., *L*-series, λ=292·2 Å.; glucinum, *K*-series, λ=118·2 Å., *L*-series, λ=428·1 Å.; lithium, *K*-series, λ=290·8 Å., *L*-series, λ=1019·0 Å. The result for the *K*-series for boron is in good agreement with that obtained by Hughes, but considerable difference occurs between the respective values for the *L*-series. The critical absorption *K*-wave-lengths for lithium represent the first two members of a series with a frequency formula given by $\nu=N(1-1/m^2)$ beginning approximately at 387·7 Å., and extending to 290·8 Å. The model of the atom put forward by Bohr makes no provision for this series. The wave-lengths for the *K*-series for glucinum would extend from about λ=157·6 Å. to λ=118·2 Å., and the configurations 4_{2_1}—4_{2_1} would appear to provide a spectral series with limits approximating to the above wave-lengths.

For the elements from potassium to glucinum, the square roots

of the critical potentials for the K-series are very closely proportional to the respective atomic numbers, but lithium, helium, and hydrogen show a departure from the linear relation. The results however, support the view that the Lyman ultra-violet series for hydrogen is the K X-ray series of this element, and also that the convergence wave-length of the K-series for helium is approximately $\lambda=485\cdot5$ Å. The Moseley law which is known to apply for the L-series of the heavier elements ceases to apply for elements lighter than argon, but a linear relationship obtained between the atomic numbers of the lighter elements and the exciting voltages of their L-series merges into the ordinary Moseley law when the element argon is reached. W. E. G.

Corpuscular Spectra and the Photoelectric Effect. MAURICE DE BROGLIE and LOUIS DE BROGLIE (*Compt. rend.*, 1922, **175**, 1139—1141).—Whiddington has stated (*Phil. Mag.*, 1922, [vi], **43**, 1126) that corpuscular rays were not observed when $h(\nu-\nu_c)$ is less than $h\nu_c$, ν being the frequency of the exciting radiation and ν_c that of the critical discontinuity c. The authors point out that under these conditions the rays are much less easy to obtain. Further, Whiddington's generalisation that the K-rays of tungsten do not excite corpuscular rays in the case of elements of atomic number greater than 50 does not appear to hold in the case of barium (Atomic No.=56), where very feeble rays were observed. This was also the case with iodine (Atomic No.=53), but no visible rays were obtained with samarium (Atomic No.=62). The variation in intensity of the corpuscular rays excited by a radiation of frequency ν is calculated; the total energy of the corpuscles composing the ray is $A\nu_c^3\frac{\nu-\nu_c}{\nu^4}$ and if ν_c is replaced by its value as a function of the atomic number, the expression may be regarded as such a function. Brillouin's theory (*Compt. rend.*, 1920, **170**, 274), introducing the idea of thermal agitation on electronic impact, is briefly discussed, and it is stated that its developments are not inconsistent with the experimental results obtained with respect to the photoelectric effect of X-rays. H. J. E.

Dielectric Constants at the Critical Temperature. W. HERZ (*Z. physikal. Chem.*, 1922, **103**, 269—272).—The author has calculated the dielectric constant of thirty-three liquids at the critical temperature. These substances at ordinary temperature have dielectric constants varying between 81·1 and 1·491. The dielectric constant at the critical temperature ought theoretically to be constant for all substances. The author finds that although the value is not constant it shows a decided tendency toward a constant value; the calculated values vary between 2·40 and 1·17. J. F. S.

The ϵ and ζ Potential at the Interface Barium Sulphate-Water. A. GYEMANT (*Z. physikal. Chem.*, 1922, **103**, 260—268).—The dependence of the ζ potential of barium sulphate on

the concentration of the barium-ions has been determined by means of *E.M.F.* measurements. The experiments lead to the conclusion that in order to explain the ζ-potential, the barium-ions and all other ions present must be taken into account. The observed dependence of the ζ potential on the concentration of barium-ions cannot be deduced from the dependence of the ϵ potential on the barium-ion concentration, when the changes of ϵ are evaluated by the method of Chapman (*Phil. Mag.*, 1913, [vi], **25**, 475), and of Herzfeld (*Physikal. Z.*, 1920, **21**, 28), in which the adsorption is neglected. J. F. S.

Curves of Electrocapillarity in Non-aqueous Solutions. H. Wild (*Z. physikal. Chem.*, 1922, **103**, 1—38).—Electrocapillarity curves have been constructed for saturated solutions of potassium chloride, potassium nitrate, mercurous nitrate, and also for nitric acid in each of the two liquid layers of the liquid pairs water and amyl alcohol, phenol, furfuraldehyde, ethyl acetate, ethyl ether, aniline, chloroform, propyl alcohol, and *iso*butyl alcohol, respectively, the whole system in each case being in partition equilibrium. The results show that two such solutions in equilibrium have the same Nernst potential $\pi_1=\pi_2$ towards a given metal. This equality is true within the limits with which the absolute potential can be deduced from the electrocapillarity curves, that is, 5—10 m.-volts. With the same accuracy, it is deduced that the tension at the interface between the two phases at equilibrium π_3 is zero or smaller than 5—10 m.-volts. This behaviour is true for all the cases examined, and can be held to be a general rule for all solvents, but the generalisation of the rule to all ions would be unsafe, for it is quite possible that the capillary active ions may behave differently in different cases, particularly in those cases where well-marked ion adsorption potentials are shown. In these cases an additional potential difference must be noticed, namely, that due to the partition of the ions. J. F. S.

Forces at the Boundary between Phases. Emil Bauer (*Z. physikal. Chem.*, 1922, **103**, 39—42).—A theoretical paper in which, on the basis of the experiments of Wild (cf. preceding abstract), the author discusses the origin of the potential difference at the boundary between two liquid phases. In an earlier paper (A., 1916, ii, 231), the author expressed the view that the potential difference was due to ion adsorption, whilst Beutner (A., 1918, ii, 214; 1919, ii, 263) maintains that a partition of the ions between the phases is the cause. The author now shows that his view is supported by the electrocapillarity measurements of Wild.

J. F. S.

Theory of Electrocapillarity. I. Electrocapillary Phenomena in Non-aqueous Solvents. A. Frumkin (*Z. physikal. Chem.*, 1922, **103**, 43—54).—Curves of electrocapillarity have been determined for 0·1*N*- and *N*-ammonium nitrate, *N*-sodium bromide, and *N*-sodium iodide in methyl alcohol, 0·2*N*-ammonium

nitrate, N-lithium chloride, and N-sodium iodide in ethyl alcohol, N-lithium chloride in mixtures of ethyl alcohol and water, $0{\cdot}9N$-lithium nitrate, $0{\cdot}5N$-lithium chloride, and N-ammonium thiocyanate in acetone, N-ammonium thiocyanate and $1{\cdot}6N$-sodium iodide in pyridine. The results show that the activity of the anion in these solutions manifests itself in exactly the same way as in aqueous solutions. The maximum in these solutions, when compared with aqueous solutions of corresponding composition, is found to be displaced to the left, that is, it corresponds with a smaller cathodic polarisation. J. F. S.

Theory of Electrocapillarity. II. A. FRUMKIN (*Z. physikal. Chem.*, 1922, **103**, 55—70; cf. preceding abstract).—It is shown that the whole of the electrocapillary phenomena are governed by the equation $d\gamma = \epsilon d\phi - \Sigma\Gamma_i d\mu_i$, where γ is the thermodynamic potential in the solution containing μ_i ions, ϕ is the potential difference of solution/metal, and Γ_i the number of ions which must be added to the solution so that μ_i remains constant when the surface of the metal is increased by a unit. The values of $d\gamma/d\phi$ and E, the quantity of electricity combined with Γ_i ions, have been determined experimentally for $2N$-sulphuric acid saturated with mercurous sulphate, E (calc.) 39×10^{-6} coul./cm.^{2}, E (obs.) 39×10^{-6} coul./cm^2.; N-sodium chloride saturated with mercurous chloride, E (calc.) 50×10^{-6} coul./cm^2., E (obs.) 47×10^{-6} coul./cm^2.; N-potassium hydroxide saturated with mercuric oxide, E (calc.) 21×10^{-6} coul./cm^2., E (obs.) 17×10^{-6} coul./cm^2.; N-potassium nitrate and $0{\cdot}01N$-potassium iodide saturated with mercurous iodide, E (calc.) 86×10^{-6} coul./cm.^{2}, E (obs.) 90×10^{-6} coul./cm.^{2}, with the results stated. It is shown that the Lippmann-Helmholtz differential equation for solutions is true both for those with normal electrocapillarity curves and for those with abnormal curves. The potential of a dropping electrode always coincides with the value given by the corresponding electrocapillarity curve. A potential difference exists between mercury on the one hand and water, methyl alcohol, ethyl alcohol, and acetone on the other when the surface layer contains either ions or adsorbed molecules of a dissolved substance. In investigations of the present type, it is necessary to differentiate between thermodynamic and electrocapillary solution tensions. J. F. S.

Decomposition Tensions of Fused Mixtures of Sodium Hydroxide with Zinc Oxide or Cadmium Oxide. L. ROLLA and R. SALANI (*Gazzetta*, 1922, **52**, 286—313).—Experiments similar to those of Sacher (A., 1902, ii, 120) have been made on mixtures of molten sodium hydroxide with zinc oxide or cadmium oxide. Fused sodium hydroxide shows two points of cathodic decomposition, the lower one, 1·20 volts, corresponding with the discharge potential of the hydrogen-ions; the higher point, corresponding with the discharge potential of the sodium-ions, has the value 2·08 volts at 460°, 2·13 volts at 412°, and 2·24 volts at 364°. With the mixtures containing zinc or cadmium oxide, the decom-

position occurring is that of zinc or cadmium hydroxide, the decomposition tensions for the zinc- and cadmium-ions being, respectively, 1·80 and 0·89 volts. T. H. P.

The Electrolytic Dissociation of Dibasic Acids. Determination of the Second Dissociation Constant of Acids from Electrometric Measurements. ERIK LARSSON (*Z. anorg. Chem.* 1922, **125**, 281—294).—The author applies the theory of Bjerrum (A., 1919, ii, 9) to the ionic equilibria in a solution which contains the neutral salt and the free dibasic acid. He shows how the second dissociation constant can be calculated from the hydrogen-ion activity measured electrometrically. The results obtained agree well with some earlier results obtained by the conductivity method. W. T.

Formic Acid. II. Electrolytic Dissociation of Formic Acid. FR. AUERBACH and H. ZEGLIN (*Z. physikal. Chem.*, 1922, **103**, 178—199).—The electrical conductivity of formic acid and of sodium formate has been determined over a wide range of concentration at 18°. It is shown in agreement with earlier investigators that small quantities of formic acid and sodium formate are decomposed at the platinised electrodes. The decomposition has been investigated and in the case of the formate shown to consist in an oxidation to sodium hydrogen carbonate and to be due to the oxygen occluded in the platinised electrodes. This disturbing factor may be removed by suitable treatment of the electrodes with hydrogen before the measurements. The limiting value of the molecular conductivity of sodium formate at 18° is extrapolated to 91, and from this value the limiting value for formic acid is calculated to be 362·5. The dissociation constant for formic acid is shown to be inconstant and to vary with increasing dilution from $2{\cdot}05 \times 10^{-4}$ to $1{\cdot}91 \times 10^{-4}$, and this difference is shown not to be due to experimental error. Formic acid belongs, therefore, to the acids of medium strength which do not follow the law of mass action closely. Values have been calculated for the electrical conductivity of formic acid which agree with the experimental values exactly, over the whole range of concentration, on the basis of Ghosh's hypothesis. J. F. S.

The Anomaly of Strong Electrolytes. HENRY J. S. SAND (*Phil. Mag.*, 1923, [vi], **44**, 129—144).—A critical examination of the theories of Ghosh (A., 1918, ii, 215, 348, 392, 790), and of Milner (A., 1918, ii, 148). Employing the Boltzmann theorem and the Born theory of the potential energy of a pair of attracting ions, estimations are made of the degree of association of a completely ionised electrolyte immersed in a medium of uniform dielectric constant. It is shown that the probability of the two ions of a binary electrolyte (N/10-solutions) being in contact in a given small volume is only 8·1 times as great as the probability of their occurrence in any two volumes of the same size so situated that the attraction between the ions is negligible. The hypothesis of complete ionisation in the case of salts like sodium chloride is

thus completely established. It is shown that a preponderating proportion of the ions will be subject to the inverse square law of electrical action.

The relation $PV=2RT-\frac{1}{3}RThf(h)$ obtained by Milner from the Clausius' virial theorem can have only approximate validity. The Ghosh theory of the "crystalline" arrangement of the ions in aqueous solutions is criticised, and it is concluded that the space lattices in this theory are merely theoretical "distributions of reference." The deductions from Ghosh's and Milner's osmotic pressure formulæ are compared with the experimental results. The agreement between the mean experimental values of $(2-i)$ for univalent binary chlorides in aqueous solutions and the same value derived from Ghosh's formula is good; the agreement at the higher concentrations is better than that attained by Milner's theory.

W. E. G.

Relationship between the Specific Heat of Liquids. W. Herz (*Z. anorg. Chem.*, 1922, **125**, 295—300).—A theoretical paper. It is shown that the specific heats of liquids at two-thirds their critical temperature divided by the values at one-half the critical temperature gives a fairly constant value. This constant for the twenty organic liquids quoted is about 0·8. Liquids in a homologous series show an increase of about 9 for the introduction of a CH_2 group, but with aniline–dimethylaniline there is an exception, the difference being very small; in this series, the specific heat decreases with increasing molecular weight. In homologous series, the molecular heat of evaporation increases about 10 for each CH_2 group, but there are many exceptions. The introduction of a chlorine atom in place of a hydrogen atom increases the molecular heat of evaporation by about 9·5 units, the introduction of a second chlorine atom has a less effect. A double bond lowers it by about two units.

W. T.

[Determination of Boiling Points.] Boiling Points of Ammonia, Sulphur Dioxide, and Nitrous Oxide. F. W. Bergstrom (*J. Physical Chem.*, 1922, **26**, 876—894).—A comparison has been made of the efficiency of single-walled and vacuum-jacketed boiling vessels. It is found that the boiling point of ammonia, determined in a single-walled vessel, is about 0·2° high, even with internal electrical heating. Determination in a Cottrell tube reduces this error. Boiling points may be determined accurately in a vacuum-jacketed vessel at temperatures as low as −90°, but in such cases a correction should be applied for the depth of immersion of the bulb, and there should be no uncooled stem. The Cottrell apparatus can be used successfully at temperatures at least as low as −33·4°. Better equilibrium between vapour and liquid is obtained and uncertain temperature corrections are eliminated by using this apparatus, and a smaller quantity of liquid is generally required. The following boiling points have been determined at 760 mm.: ammonia, −33·41°±0·1°, sulphur dioxide, −10·02°±0·1°, and nitrous oxide, −89·5°±0·2°.

J. F. S.

Application of the Method of Continuous Variations to Ebullioscopic Phenomena for the Determination of Double Salts in Solution. F. BOURION and E. ROUYER (*Compt. rend.*, 1922, **175**, 1406—1408).—The method of continuous variations as applied to ebullioscopic measurements was tested in the case of solutions of cadmium chloride with potassium chloride and ammonium chloride, respectively, and solutions of cadmium iodide with potassium iodide, and found to give quite as satisfactory results as when applied to cryoscopic measurements. W. G.

A Micro-method for the Determination of Molecular Weight in a Melting-point Apparatus. II. Determinations with Extremely Minute Quantities. KARL RAST (*Ber.*, 1922, **55**, [*B*], 3727—3728).—The author has succeeded in further refining his micro-method for the determination of molecular weight in freezing camphor to such an extent that it is possible to obtain accurate results with scarcely visible amounts of substance. The capillary tube is slightly conical in shape, and rather wider (2—3 mm.) than those recommended previously; it is essential that it should be very thin in the wall and that the bottom should be hemispherical. The solutions are prepared in the capillary itself, the substance under investigation being first introduced and subsequently the camphor. The materials are pressed together by a small glass rod. The capillary is sealed and subsequently drawn out to a long thread, by means of which it is attached to the thermometer. Mixing of the components is effected by melting and re-solidification. The column in the capillary must not be more than 2 mm. in height so that in general 0·2—0·3 mg. of substance and 2—3 mg. of camphor are required. It is essential to guard against undue concentration of the solutions, which, however, may sometimes be greater than normal. H. W.

The Influence of the Velocity of Cooling on the Hardness and Microstructure of Eutectic Mixtures. N. S. KURNAKOV and A. N. ACHNASAROV (*Z. anorg. Chem.*, 1922, **125**, 185—206).—The hardness of eutectic mixtures increases with the rate of cooling and with the degree of fineness of the grains. This tendency to increase in hardness decreases with increasing brittleness, *e.g.*, zinc-antimony. Increasing fineness of grains also results in increasing passivity of the alloy. Homogeneous phases of pure metal and solid solutions show no change in hardness on rapid cooling. The above conclusions were obtained from a study of the systems cadmium-silver, silver-copper, gold-nickel, zinc-antimony. W. T.

General Theory of the Adsorption of Solutions. BROR. GUSTAVER (*Kolloid Z.*, 1922, **31**, 358—362).—A theoretical paper in which the author criticises the views put forward on the adsorption of solutions by Ostwald and Izaguirre (A., 1922, ii, 480). It is shown that the theory is not in keeping with the author's results on the sorption of vapours by charcoal (A., 1922, ii, 479), neither is

it in keeping with respect to the thickness of the adsorbed layer as determined by the author and others. J. F. S.

Adsorption of Ions by Freshly Precipitated Manganese Dioxide. P. B. GANGULI and N. R. DHAR (*J. Physical Chem.*, 1922, **26**, 836—844).—The authors have investigated the adsorption of kations by manganese dioxide, and also the effect of various anions on the adsorption. Manganese dioxide was prepared in the solution of ions under investigation by the addition of equivalent quantities of potassium permanganate and manganous sulphate and the amount of adsorption determined by analysing the filtered solution after equilibrium had been reached. Some thirty-five salts have been used in the investigation, and the results show that the coagulating powers of the different electrolytes as calculated from the percentage of kation adsorbed from approximately normal solutions of the electrolytes follow the Schulze-Hardy law very imperfectly. The effect of the anions on the adsorption of kations by manganese dioxide is found to be very marked. There is, however, no regularity in the variations shown by the adsorption values of the kations with variation of the anion. In the case of ferric salts, the adsorption of ferric-ions by manganese dioxide is abnormally large; a result which is probably to be attributed to a partial hydrolysis of the ferric salt with the separation of ferric hydroxide. Among the electrolytes of metals occurring in the same group of the periodic system, the values of the percentage adsorption are generally found to be in the order of the atomic weights of the kations. J. F. S.

Physical Chemistry of Dyeing. Acid and Basic Dyes. T. R. BRIGGS and ARTHUR W. BULL (*J. Physical Chem.*, 1922, **26**, 845—875).—The process of dyeing wool with acidic and basic dyes has been investigated from the point of view of the adsorption hypothesis as formulated by Pelet-Jolivet and Bancroft (*Applied Colloid Chemistry*, 1921, 115). The effect of dyes on the adsorption of acids by wool and of acids on the adsorption of dyes has been determined quantitatively for typical acid dyes. It is shown that the taking up of dyes is a case of adsorption and that the amount of dye adsorbed varies continuously with a change in the hydrogen-ion concentration of the dye-bath. No evidence of chemical action between dyes and wool has been obtained.

J. F. S.

The Determination of the Dissociation Pressures of Hydrated Salts by a Dynamical Method. II. JAMES RIDDICK PARTINGTON and DONALD BENNETT HUNTINGFORD (T., 1923, **123**, 160—170).

A New Explanation of Diffusion. ALEXANDR BATĚK (*Chem. Listy*, **16**, [9], 295—299).—Fick's theory for the diffusion of liquids (*Ann. Phys. Chem.*, 1855, [ii], **94**, 59) is discussed, and its experimental basis questioned. Certain discrepancies between

ne results calculated on this theory and those obtained experimentally by Voit (*Ann. Phys. Chem.*, 1867, [ii], **130**) are pointed ut. The technique of optical methods for the determination of ates of diffusion is examined, and possible sources of error are uggested. Weber's confirmation (*Ann. Phys. Chem.*, 1870, [iii], , 469, 536) of the applicability of Fourier's law to the diffusion f liquids is shown to be doubtful, and the necessity for a reconideration of the whole question emphasised. The mechanism of he diffusion of liquids is then discussed from first principles, and he use of the conception of limiting states of solutions in helping o elucidate the problems of diffusion of liquids is substantiated.

R. T.

Diffusion in Solid Solutions. H. Weiss and P. Henry *Compt. rend.*, 1922, **175**, 1402—1405).—A study of the interpenetration, by diffusion, of gold and silver at the temperatures 935°, 885°, and 835° shows that the form of the law of diffusion n fluids is valid. The values of the constant K at the temperatures used, when interpolated to 870°, give a value 0·0000375, which is n very close agreement with the value obtained by Fraenkel and Houben (A., 1921, ii, 491). W. G.

Process of Diffusion in Gelatin. Liesegang's Phenomenon. Carl Adolf Schleussner (*Kolloid Z.*, 1922, **31**, 347—352).—With the object of employing the diffusion into gelatin as a means of testing the suitability of various specimens of this substance for use in the manufacture of photographic plates, the author has examined the conditions under which the Liesegang rings are produced. It is shown that for a regular and uniform diffusion the gelatin must be in a uniform condition. The necessary condition can only be obtained after the gelatin has been held in solution for at least twenty-four hours. It is shown that from the character of the ring formation conclusions may be drawn as to the purity of the gelatin. The intermediate rings which may be observed with a lens between the main rings are shown to be silver salts of phosphoric and halogen acids and are due to impurities in the gelatin. A bibliography of the work on the formation of Liesegang rings and allied phenomena is included in the paper. J. F. S.

The Relation between the Crystal Structure and the Constitution of Carbon Compounds. I. Compounds of the Type CX_4. Isabel Ellie Knaggs (T., 1923, **123**, 71—79).

Double Compounds and Mixed Crystals. Racemates and Pseudo-racemates. Philippe Landrieu (*Bull. Soc. chim.*, 1922, [iv], **31**, 1217—1241).—Lectures delivered at the Collège de France. G. F. M.

Hydrogen-ion Concentration and the Properties of Emulsoid Colloids. Robert Herman Bogue (*J. Physical Chem.*, 1922, **26**, 801—811).—A theoretical paper in which it is shown that the various physical properties of the emulsoid colloids, including

the viscosity, jelly strength, melting point, and joining strength, are at a minimum at a hydrogen-ion concentration corresponding with the isoelectric point. As the acidity or alkalinity of the solution is increased from this point, the whole of these properties increase in value. It is shown that salt precipitations for gelatin contents should be made at the isoelectric point if the maximum precipitation is to be obtained. The necessity for a careful control of the hydrogen-ion concentration in investigations on the proteins is emphasised, and the desirability of a similar control in the gelatin and glue plant during manufacture is also pointed out. The limitation of the benefit obtainable from such control, however, makes the practicability of such methods, when applied to the improvement of the quality of the material, very questionable. The estimation of the hydrogen-ion concentration is urged as a test in the evaluation of gelatin and glue, but it is not recommended that all tests of viscosity, jelly strength, and joining strength be made at a specified hydrogen-ion concentration. J. F. S.

Present Position of the Theory of Peptisation. W. MOELLER (*Z. Leder Gerb. Chem.*, 1922, **1**, 360—376; cf. A., 1915, i, 439).—A theoretical paper in which the author discusses the theory of peptisation, particularly in connexion with its application to tanning and the leather industry. It is shown that the mechanism of tanning consists in the destruction of the sol-condition of the peptised solution by the substance of the hide. The hide substance removes the sol by adsorbing the peptising agent, and the separated coagulated oil surrounds the micellæ of hide to form micro-crystals. The author defines tan as a system which of itself is quite insoluble, but by peptisation may be converted into a colloidal solution. Leather is defined as an animal hide the elementary particles of which are crystalline micellæ protected by a sheath of tan particles from hydrolytic influences. J. F. S.

Protective Colloids. XII. Gelatin as a Protective Colloid. III. Colloidal Platinum. A. GUTBIER and A. ZWEIGLE (*Kolloid Z.*, 1922, **31**, 346—347; cf. A., 1922, ii, 485).—Solid platinum colloids may be prepared by reducing chloroplatinic acid in aqueous chloroform solution by means of hydrazine hydrate in the presence of solutions of gelatin. When five parts of a 1% solution of chloroplatinic acid in water saturated with chloroform is mixed with five parts of 0·14% gelatin solution and slowly reduced by the addition of 0·1% solution of hydrazine hydrate, a colloidal solution which is black by transmitted light and dark brown by reflected light is produced. This sol on keeping deposits a small quantity of a black powder, and on dialysis yields a very stable sol. The black precipitate is reversible to the extent of about 70%. The sol is stable towards heat and quite insensitive to electrolytes which are capable of producing an hydroxyl-ion. Solutions of neutral salts coagulate the sol *only* after keeping for several days, whilst acids, even in dilute solution, produce a rapid coagulation. On evaporation at 27° in a vacuum over sulphuric acid, a solid

colloid is obtained which is completely reversible in cold water and contains 18·76% of platinum. When the quantities of the reagents employed are one part of 0·14% gelatin, five parts of 0·1% solution of chloroplatinic acid, and four parts of chloroform water, the solid sol obtained by the same process is also completely reversible to form stable secondary sols in dilute solution, and the solid itself contains 55·67% of platinum. J. F. S.

Validity of the Law of Mass Action for Ionic Equilibria. J. N. Brönsted and Kai Pedersen (*Z. physikal. Chem.*, 1922, **103**, 307—315).—The reaction between ferric chloride and potassium iodide has been investigated in aqueous solution at 25°, and from the results it is shown that the law of mass action is valid for ionic equilibria when these are set up in concentrated salt solutions as solvents. A convenient method for determining solubility in the absence of air is described and used to determine the dissociation constant of the tri-iodide-ion. The value for the equilibrium constant of the dissociation $I_3' \rightleftharpoons I_2 + I'$ at 25° is 0·00611, at 15·0°, 0·00502, and at 18·5°, 0·00540. J. F. S.

Formic Acid. III. Partition of Formic Acid between Ether and Water and its Application to Analytical Purposes. Fr. Auerbach and H. Zeglin (*Z. physikal. Chem.*, 1922, **103**, 200—237).—The partition coefficient of formic acid has been determined at 18° for ether and water, 0·5*N*-sulphuric acid, and 0·5*N*-sulphuric acid containing 100 g. of sodium chloride per litre, respectively. In the case of ether and water, the coefficient was determined for concentrations up to 1 mol. per litre, and in spite of corrections for the electrolytic dissociation of the formic acid in water the partition coefficient of the undissociated acid was found to be inconstant, but to vary in a linear manner with the concentration in the aqueous phase; the value $f=C_a/C_w$ varies from 0·395 for $C_w=0·0446$ to 0·454 for $C_w=1·343$. In the case of ether and 0·5*N*-sulphuric acid, in which the electrolytic dissociation in the aqueous phase is practically zero, the partition is displaced in favour of the ether layer, but here also the coefficient is dependent on the concentration of the aqueous layer. Sulphuric acid containing sodium chloride gave similar results to the acid and ether alone. The progression of the partition coefficient is explained by the polymerisation of the formic acid in ethereal solution. From the law of mass action the extent of the polymerisation is calculated on the assumption of double molecules by means of the formula $x=[(HCO_2H)_2]/[HCO_2H]^2$; the following values of x are obtained: for ether saturated with water, $x=0·139$; for ether saturated with 0·5*N*-sulphuric acid, $x=0·147$, and for ether saturated with 0·5*N*-sulphuric acid containing 100 g. of sodium chloride per litre, $x=0·158$. The small differences in the polymerisation constant are due to the varying water content of the aqueous phase. The true partition coefficients have been calculated from the above-mentioned quantities and the experimental results. The partition coefficient of undissociated unimolecular formic acid

at 18° has the following values: between ether and water, $f_0=0·393$; between ether and $0·5N$-sulphuric acid, $f_0=0·398$, and between ether and $0·5N$-sulphuric acid containing 100 g. of sodium chloride per litre, $f_0=0·400$. For the purpose of applying the partition coefficient to analytical purposes, the volume changes of the phases when ether is shaken with water or $N/2$-sulphuric acid solution were either determined or taken from the unpublished work of Mylius. By means of the volume correction factor and the partition coefficient, the concentration of formic acid in a $0·5N$-aqueous sulphuric acid solution may be calculated from the concentration in the ethereal layer after shaking the sulphuric acid solution with ether. Equations for this calculation have been derived, and tables of numerical factors are given in the paper. Formic acid in $0·5N$-sulphuric acid solutions may be estimated by this method for amounts of formic acid between 2·4 g. and 0·011 g. with an average error of 0·38%. If the sulphuric acid also contains 100 g. of sodium chloride per litre, the average error of the estimations is 0·26%. J. F. S.

Velocity Law of Unimolecular Reactions. J. A. Christiansen (*Z. physikal. Chem.*, 1922, **103**, 91—98).—A theoretical paper in which on the assumption that only molecules in a definite quantic condition react, the author has developed a velocity formula for reactions of the type $AB \longrightarrow A+B$. The equation deduced has the form $k=(p_m/p_n)e^{-(\epsilon_m-\epsilon_n)/RT}\,.\,\nu'/(1-e^{-h\nu'/RT})$, where k is the velocity constant, p_m and p_n are the a priori probabilities, respectively, that the molecules are in the m-quantic or normal condition when the m-quantic condition is that necessary for reaction; the other symbols have their usual significance; those with the dash, such as ν', refer to the products of the reaction. The author shows that when $h\nu'/RT$ is small the equation reduces to the form $k=(p_m/p_n)\times e^{-(\epsilon_m-\epsilon_n)/RT}\cdot RT/h$, which is practically the same as the expression deduced by Herzfeld (A., 1922, ii, 136) from Stern's expression for unimolecular reactions. When $h\nu'/RT$ has a comparatively large value, the expression reduces to $k=(p_m/p_n)\,.\,e^{-(\epsilon_m-\epsilon_n)/RT}\times\nu'$ which is the same as the expression obtained by Dushman (A., 1921, ii, 315). J. F. S.

Thermal Decomposition of Carbonyl Chloride. J. A. Christiansen (*Z. physikal. Chem.*, 1922, **103**, 99—138).—The thermal decomposition of carbonyl chloride, both alone and mixed with chlorine, has been investigated at a number of temperatures between 655° and 782° absolute. The results indicate that over the range of temperature 705—745° Abs. the reaction takes place according to the equation $h=k\sqrt{C_{Cl_2}}(C_{COCl_2}-\xi)$, where h is the velocity, k a constant, and $\xi=C_{CO}\,.\,C_{Cl_2}/K$, K is the equilibrium constant of the reaction $COCl_2 \rightleftharpoons CO+Cl_2$. The equation only holds when the concentration of the carbonyl chloride, carbon monoxide, and chlorine are of the same order (10^{-3}—10^{-4} mol./litre). At the commencement of the reaction, that is, until the above condition obtains, the divergences from the equation are always positive,

in the sense that the observed velocity is always greater than the value calculated according to the above equation. The velocity is not markedly affected by a change in the relative glass surface in the ratio 50/38. The velocity is unaffected by the presence of air when the concentrations of carbon monoxide and chlorine are considerable from the commencement of the reaction. When it is assumed that the expression for the velocity does not change with temperature, the value of the constant k can be found by means of the expression $\log k = -11420/T + 15{\cdot}154$ for the temperature range 685—782°. An experiment at 655° was found to be less exact, but it agreed with the above expression within the limits of the experimental error. J. F. S.

The Velocity of Reaction in Mixed Solvents. IV. The Influence of the Base on the Velocity of Saponification of Esters. ALBERT ERIC CASHMORE, HAMILTON McCOMBIE, and HAROLD ARCHIBALD SCARBOROUGH (T., 1923, **123**, 197—207).

Chemical Kinetics of Heterogeneous Systems. IV. The Mechanism of Chemical Reaction, when Noble Metals Dissolve in Potassium Cyanide Solution. EIICHI YAMAZAKI (*J. Chem. Soc. Japan*, 1922, **43**, 686—690).—According to Bodländer (*Z. anorg. Chem.*, 1896, **19**, 583), gold and other noble metals dissolve in potassium cyanide solution owing to the catalytic action of hydrogen peroxide produced as an intermediate; but this explanation and Bodländer's formulæ cannot explain the author's experiences. The reaction velocity is approximately proportional to the square root of the concentration of oxygen, but not to the concentration itself. The production of hydrogen peroxide is a secondary reaction, which may, of course, accelerate the dissolution of the metals and produce the peroxides, when $Ba^{\cdot\cdot}$ or $Ca^{\cdot\cdot}$ are present in the solution. When the dissolution of the metal is normal, the reaction proceeds as follows: $Ag = Ag^{\cdot} + \ominus$; $O + 2\ominus \longrightarrow O''$; $H_2O + O'' \longrightarrow 2OH'$; or $2Ag + H_2O + \frac{1}{2}O_2 = 2Ag^{\cdot} + 2OH'$, etc. K. K.

Some Properties of the Active Nickel used as Catalyst in Organic Chemistry. ANDRÉ BROCHET (*Compt. rend.*, 1922, **175**, 1073—1075; cf. this vol., ii, 18).—The pyrophoric property of nickel prepared for use as a catalyst is entirely due to occluded hydrogen, and if the metal is freed from that gas under conditions which maintain in the nickel the property of being readily transformed into oxide, its catalytic activity remains unimpaired. There is no relation between the pyrophoric condition and the catalytic efficiency, although the extent of the former is a convenient indication of the progress of the preparation of the catalyst. Catalytic nickel if washed and dried loses its pyrophoric property; in cases in which the catalytic activity is affected by this operation, it may be restored by heating for a short time in hydrogen. The author appends a brief discussion, from the point of view of employment as a catalyst, of the extent and condition of the metallic surface and the property of occluding hydrogen. H. J. E.

Catalytic Hydrogenation with Nickel. Factors Determining Catalytic Activity. R. THOMAS (*J. Soc. Chem. Ind.*, 1923, **42**, 21—26T).—A description is given of some of the methods which may be employed for the preparation of catalytically active nickel, and the relative activities of variously prepared nickel catalysts in the hydrogenation of oils have been determined. The most active catalyst was that obtained by the reduction by means of hydrogen at 350—500° of nickel hydroxide precipitated on kieselguhr. A nickel catalyst prepared by reduction with charcoal at 600°, or by electrical disintegration, or by the decomposition of nickel carbonyl was less than one-fourth as active, whilst nickel precipitated from its salts by means of aluminium showed only about one-sixth of the activity. The author concludes with a theoretical discussion as to what are ultimate factors which influence catalytic activity, and what form of energy transference occurs between the catalyst and reacting substances. It is suggested that the catalyst activates a certain number of molecules of the reactants by thermionic emission, and that the bulk of the molecules are then successively activated by electron emission from molecules already in an activated condition through the instrumentality of the catalyst. G. F. M.

Heterogeneous Catalysis and the Orientation of Adsorbed Molecules. H. R. KRUYT and C. F. VAN DUIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **25**, 324—326).—In continuation of previous work (A., 1921, ii, 392), the authors find that the reaction between aqueous solutions of dibromosuccinic acid (meso- or racemic form) and potassium iodide is considerably accelerated in the presence of charcoal. The greater acceleration occurred in the case of the meso-form, a result in accord with stereochemical considerations. The result confirms the conclusion that positive contact catalysis is to be anticipated only when the reacting group of molecules is directed away from the adsorbent and towards the surrounding medium. J. S. G. T.

A Type of Ideal Electric Atoms. J. L. (*Nature*, 1922, **110**, 873).—The mathematical solutions arrived at by Hargreaves (this vol., ii, 19) give a possible structure for an ideal atomic nucleus of the Rutherford type. A. A. E.

Speculation Concerning the Positive Electron. HORACE H. POOLE (*Nature*, 1923, **111**, 15—16).—Lodge's speculation (A., 1922, ii, 836) is examined from the point of view of the relative abundance of the lighter and heavier elements, the case of hydrogen being considered in particular. An immense discrepancy is apparent. Doubtless, some negative protons would combine with previously formed positive complexes, but since about half the complex nuclei first formed would be negative, so that some of the positive protons would be lost by combination with them, these effects would be expected to balance approximately. If, however, it is assumed that when two unequal nuclei combine, the

sign of the combination is determined by that of the larger constituent, it is conceivable that if the first set of nuclei formed happened to be positive, they might so direct the course of subsequent events as to lead to the existing distribution of the elements. A. A. E.

A Laboratory Apparatus for Rapidly Drying Sensitive Organic Substances. J. BOUILLOT (*J. Pharm. Chim.*, 1923, [vii], **27**, 23—28).—A tube of glass, 15 cm. long and 30 mm. wide, sealed at one end and fitted with a heat-resistant cork at the other, carries the substance to be dried in a boat. The tube has two slightly narrower tubes attached vertically to its upper surface by narrow necks containing plugs of cotton wool, and in the openings of these tubes are fitted corks carrying narrow glass tubing terminated inside, by being drawn out, in narrow hooks, so as to avoid violent currents of air impinging on the boat below. The whole apparatus can be immersed in an air-bath at the required temperature, and currents of dried air can be aspirated over the contents of the boat at any required pressure. H. K.

A Simple Check Valve. J. F. BREWSTER (*J. Ind. Eng. Chem.*, 1923, **15**, 32).—A solid rubber stopper is cut about three-quarters through at the small end so that a thin flap of rubber is left to serve as the valve leaf. The stopper is then bored, leaving the flap intact, to receive a short length of glass tubing which is pushed through to within a few mm. of the valve seating. A piece of glass tubing of such diameter as to allow free play of the valve flap, but at the same time to fit the stoppers tightly, is closed at one end by the valve stopper and at the other by a one-hole stopper. The contrivance will allow the passage of air or liquid from the direction of the valve stopper to the one-hole stopper, but not in the reverse direction, and is useful for preventing, amongst other things, a "suck back" of water from a water vacuum pump into the apparatus during a vacuum distillation, etc. G. F. M.

Inorganic Chemistry.

A Convenient Method for the Preparation of Aqueous Hydrobromic Acid of Constant Boiling Point. J. G. F. DRUCE (*Chem. News*, 1923, **126**, 1).—The method described by Pickles (A., 1919, ii, 411) gives rather a dilute acid, and the distillation is difficult to carry out without "bumping" taking place. The following modification obviates the latter difficulty and gives a distillate containing more than 48% of hydrogen bromide: 10 c.c. of strong sulphuric acid are added to a solution of 15 g. of potassium bromide and 0·2 g. of stannous chloride in 25 c.c. of water. After remaining over-night, the clear liquid is decanted from the crystals of potassium hydrogen sulphate which have

separated, and distilled, the fraction coming over between 120° and 125° being collected. The yield is more than 90% of the theoretical, and the product contains only a trace of chlorine.

A. R. P.

The Structure of the Sulphur Dioxide Molecule. A. O. RANKINE and C. J. SMITH (*Proc. Physical Soc.*, 1922, **35**, 33—38).—The authors' method of determination of the molecular dimensions of gaseous molecules from viscosity measurements (A., 1921, ii, 192) has been employed to decide between the relative merits of two formulæ for sulphur dioxide. That proposed by Langmuir, O=S—O, should possess the dimensions of a neon–argon–neon complex with the components arranged in a line, or arranged so that the lines joining the neon to the argon atoms make an angle of 135°. The calculated mean collision area of this model is considerably in excess of that deduced from viscosity measurements, 0.94×10^{-15} cm.². On the other hand, the calculated value for $S\langle{}^{O}_{O}$ is 0.99×10^{-15} cm.², which is in much closer agreement with experiment.

W. E. G.

Formation of Sulphur Dioxide from the Sulphates of the Alkaline Earths and Iron or Iron Sulphide. F. MARTIN and O. FUCHS (*Z. anorg. Chem.*, 1922, **125**, 307—348).—The authors found that the alkaline sulphates on being heated with metallic iron are completely reduced to the sulphides; this reduction begins at temperatures lower than that required in the case of coal. The reduction is complete in half an hour at 750° for calcium sulphate, at 850° for strontium sulphate, and at about 950° for barium sulphate. In the presence of insufficient iron and at about 150° higher, a rapid evolution of sulphur dioxide takes place. The best conditions for this are, for calcium sulphate the mixture $16CaSO_4+15Fe$, giving 80% of the theoretical yield of sulphur dioxide; for strontium sulphate the mixture $9SrSO_4+8Fe$, giving an 88·9% yield. These reactions lead to the formation of well defined ferrites, $3CaO,2Fe_2O_3=Ca_3Fe_4O_9$; $2SrO,Fe_2O_3=Sr_2Fe_2O_5$, and $BaO,Fe_2O_3=BaFe_2O_4$. Too little iron leads to the formation of alkaline-earth sulphide, too much iron gives also iron sulphide. Sulphur dioxide is also evolved by heating the alkaline-earth sulphates with iron sulphide; this can be carried out commercially by using pyrites to which has been added a little iron oxide.

W. T.

Catalytic Hydrogenation of Sulphurous Anhydride. (MLLE) MARGARET G. TOMKINSON (*Compt. rend.*, 1923, **176**, 35—36).—When a mixture of dry sulphur dioxide and dry hydrogen is passed over finely divided nickel or over nickel sulphide at 400—450°, a mixture of water vapour, hydrogen sulphide, and sulphur is obtained, and if the gases are passed sufficiently slowly the whole of the sulphur dioxide is decomposed. Cobalt sulphide, and, to a lesser degree, ferrous sulphide, may also be used as catalysts for the hydrogenation.

W. G.

Preparation of Sulphuryl Chloride. LÉONCE BERT (*Bull. Soc. chim.*, 1922, [iv], **31**, 1264—1270).—Ruff's method (A., 1902, ii, 13), consisting in boiling chlorosulphonic acid with about 1% of mercury or mercuric sulphate, is the most practical process for the laboratory preparation of sulphuryl chloride, the operation being conducted under a reflux condenser kept at about 70°, in order to return unchanged chlorosulphonic acid to the flask. For the successful conduct of the process, attention must be directed to the following important, but hitherto unpublished, points. To prevent risk of fracture, the tube of the reflux condenser should be of iron connected with the neck of the flask with a stopper of asbestos paper and silicate cement, which resists the action of chlorosulphonic acid admirably. The top of the iron tube is connected by means of asbestos thread and silicate to a short glass tube leading to a condenser and receiver for the sulphuryl chloride. The reaction does not proceed so rapidly as Ruff asserted (*loc. cit.*), and slows down considerably in the latter stages. In one hour a 40% yield, in three hours 60%, and six hours 75·8% yield was obtained, and for this reason, when considerable quantities of sulphuryl chloride are required, it is preferable to collect for one hour only and then change the flask for another containing a fresh charge of chlorosulphonic acid. The latter is conveniently obtained by saturating 70% fuming sulphuric acid with hydrogen chloride, and distilling. G. F. M.

Phosphorus. ALFRED STOCK (*Z. anorg. Chem.*, 1922, **125**, 228—234).—A theoretical paper in which the paper of Marckwald and Helmholtz (A., 1922, ii, 845) is criticised. The author points out that the melting point of phosphorus depends to a very large extent on the rate of heating. W. T.

Boron Hydrides. MAURICE L. HUGGINS (*J. Physical Chem.*, 1922, **26**, 833—835).—The author criticises the view held by Stock that boron in the boron hydrides is quadrivalent, and puts forward structures for the hydrides B_2H_6, B_4H_{10}, B_6H_{12}, $B_{10}H_{14}$, in which boron is regarded as tervalent. These structures are strikingly like those adopted for ethylene, butadiene, benzene, and naphthalene, respectively. The hydrogen atoms are held by means of four-electron bonds, such as often exist, at least temporarily, in unsaturated organic compounds. Each such four-electron bond is surrounded by four atoms. J. F. S.

Preparation of Boron Chloride. C. MAZZETTI and F. DE CARLI (*Atti R. Accad. Lincei*, 1922, [v], **31**, ii, 119—120).—Almost quantitative yields of boron chloride were obtained by passing dry chlorine through a porcelain tube containing ferro-boron heated at about 500°. T. H. P.

Silicon Hydrides. XI. The Action of Oxygen on SiH_4 and Si_2H_6. ALFRED STOCK and CARL SOMIESKI (*Ber.*, 1922, **55**, [*B*], 3961—3969).—The oxidation of the simplest hydrides of silicon has been studied in the hope that the reaction would provide

a more convenient method of obtaining compounds of the types $SiH_3·OH$, SiH_2O, than is afforded by the hydrolysis of the halides. As oxidising agents, oxygen, air, and mixtures of nitrogen and oxygen containing less of the latter than air have been used. The violence of the reaction is moderated by very slowly adding the oxidising agent to an excess of the gaseous hydride under greatly diminished pressure and at a temperature varying between $-70°$ and $-140°$. Measured volumes of the reagents are employed and the nature of the volatile products is elucidated by the authors' vacuum process. The necessary apparatus is fully figured and described in the original text. Reaction invariably occurs immediately and, in spite of the precautions described above, is frequently explosive. The products consist of unchanged hydride (including SiH_4 during the oxidation of Si_2H_6), nitrogen (and argon) when air or artificial mixtures of nitrogen and oxygen are used (the oxygen is invariably consumed completely), a considerable quantity of free hydrogen, water, and, in certain cases, small quantities of volatile silicon compounds formed during the oxidation. In addition, a colourless, non-volatile residue which generally contains brown particles is produced. This consists partly of compact crusts formed near the point of entry of the oxidising agent, partly of a fog in the interior of the reaction vessel, and partly of a uniform, vitreous deposit on the whole wall of the vessel. The colourless components are fairly readily dissolved by very dilute alkali and appear to consist of substances such as polymeric prosiloxan $(SiH_2O)_x$, silicoformic anhydride, $[(SiHO)_2O]_x$, etc.; the brown components contain silicon and possibly highly condensed silicon hydrides poor in hydrogen; they appear to be formed chiefly when the action is accompanied by considerable local heating and a deficiency of oxygen.

In spite of variation in the temperature and in the degree of dilution of the oxygen, the reaction occurs fairly uniformly. The oxidation proceeds beyond the stage $SiH_3·OH$, since the presence of $(SiH_3)_2O$ in more than traces could not be established and the stability of the gas is such that it could not have escaped detection. The main derivatives of silicon produced during the oxidation are the polymeric forms of SiH_2O, $OH·SiHO$, $SiO(OH)_2$, etc. The water is regarded as produced from hydroxylated silicon compounds which become decomposed as the temperature is allowed to become atmospheric, thus $SiH_2(OH)_2 \longrightarrow SiH_2O+H_2O$. The liberation of free hydrogen is surprising. In those cases in which elementary silicon is deposited, a part of it is doubtless due to the thermal decomposition of monosilane. Its production is not due to a secondary hydrolysis of silane, or its primary oxidation products by water formed during the reaction. It appears to be a primary product of the oxidation: $SiH_4+O=SiH_2O+H_2$; a reaction of this type is unusual and apparently due to the preponderating affinity of silicon for oxygen.

The production of hydrogen accounts for the peculiarities observed during the combustion of silicon hydrides, which differs markedly in its violence from similar cases of spontaneous ignition such as

the quiet inflammation of phosphorus hydride. The process consists of the following successive steps: inception of oxidation, liberation of hydrogen, formation of a mixture of oxygen and hydrogen, and ignition of the latter when the temperature has been raised sufficiently by the heat of the reaction. H. W.

Theory of the Structure and Polymorphism of Silica. ROBERT B. SOSMAN (*J. Franklin Inst.*, 1922, **194**, 741—764).—A theory of the molecular structure of the various forms of silica is advanced. It is suggested that the silica atom-triplet maintains a certain degree of individuality in its amorphous and crystalline states, as well as in its compounds, and the freedom of the oxygen atoms to change their positions with respect to the silicon is restricted. The triplets are assumed to assemble into chains or threads in the liquid and glassy states, and a thread structure persists in the crystalline states. The three principal crystalline modifications (cristobalite, tridymite, quartz) are built up by combining the threaded triplets in three different ways, the connexion between the threads being through the oxygen atoms, and it is maintained by the sharing of electrons. The high-low (α—β) inversions in all the forms are thought to be due to the same underlying mechanism, namely, a change in the state of motion of certain electron orbits, resulting from increased thermal vibration of the atoms, whereby the shape of the silica triplet and the relative positions of the two oxygen atoms are suddenly altered. The theory gives a satisfactory explanation for many silica phenomena, such as the minimum in the temperature–volume curve of silica glass, the relation between the specific heats of the crystalline forms, the fact that natural quartz formed at a high temperature is always homogeneous, whilst low-temperature vein quartz is right- and left-twinned, etc. G. F. M.

The Constitution of the Silicates. G. TAMMANN (*Z. anorg. Chem.*, 1922, **125**, 301—306).—The author finds that the molecular specific heats of the silicates are additive, and concludes that the molecules are independent and at temperatures far removed from their melting point do not vibrate appreciably. This conclusion is supported by the fact that only in the neighbourhood of the melting point do isomorphous complex substances diffuse into one another visibly. In solution, silicates undergo hydrolysis, and this therefore gives no definite information as to the molecules which exist in the solid. The structure of molten silicates cannot be investigated. The complex silicates differ from the carbon compounds in that they are decomposed in solution and in the fused state, and the molecular theory of organic chemistry finds no application in the chemistry of silicates. W. T.

The [Suggested] Formation of Helium and Neon in Discharge Tubes containing Hydrogen. A. PIUTTI and E. BOGGIO-LERA (*Mem. Accad. Lincei*, 1921, [v], **13**, 687—701).—Full details of work a summary of which has already appeared (cf. Piutti, this

vol., ii, 20, and also Piutti and Cardoso, A., 1920, ii, 311; Baly, *Annual Report*, 1914, 45; 1920, 29, 30). T. H. P.

The Rectilinear Diameter of Neon. E. MATHIAS, C. A. CROMMELIN, and H. KAMERLINGH ONNES (*Compt. rend.*, 1922, **175**, 933—935).—The density of neon was studied between its critical temperature (−228·71°) and its normal boiling point (−245·92°). From the experimental values obtained, the angular coefficient of the diameter was found to be $\alpha = -0.00716146$, a notably high figure. At the critical temperature the critical density is calculated to be $d_c = 0.4835$, whilst the critical coefficient is $(RT_c d_c)/p_c = 3.249$, the smallest value yet obtained experimentally with the exception of that for helium. The general conclusion is drawn that neon follows the law of rectilinear diameter.

H. J. E.

Electrical Preparation of Solid Alkali Amalgams in Quantity. PAUL M. GIESY and JAMES R. WITHROW (*J. Ind. Eng. Chem.*, 1923, **15**, 57—60).—Kerp's method (A., 1898, ii, 516; 1900, ii, 656) for the electrical preparation of amalgams can be much simplified and improved by allowing the mercury at the bottom of the cell as well as that from the flowing jet to receive current. In this way, the current can be increased to a very great extent with a corresponding reduction in manipulation and in the time of the run. If the current be led out at the tip of the jet tube a single jet tube with a stop-cock can be used instead of the changeable jets used by Kerp. It was also found that it is not necessary to work in an atmosphere of hydrogen in order to produce a pure product. Smith and Bennett's method (A., 1909, ii, 663; 1910, ii, 500) can be improved by strongly cooling the electrolyte when used for the preparation of sodium amalgam, and also by forcing the current. If a suitable diaphragm could be found which was unacted on by solutions of alkali hydroxides, or by the amalgams themselves, and, whilst offering a low electrical resistance, was a non-conductor, Shepherd's method (A., 1903, ii, 210) would undoubtedly be the best, but no suitable material could be found. It is pointed out, in conclusion, that all solid alkali metal amalgams are lighter than mercury, and not heavier, as recorded by Kerp. G. F. M.

Isomorphism of Potassium Fluoborate and Permanganate. FERRUCCIO ZAMBONINI (*Atti R. Accad. Lincei*, 1922, [v], **31**, ii, 67—73).—The author claims priority over Barker (T., 1912, **101**, 2484) for his discovery of the isomorphism between potassium fluoborate and perchlorate (*Z. Kryst. Min.*, 1905, **41**, 60). In order to ascertain whether alkali fluoborates are isomorphous with, or merely exhibit crystallographic relations towards, alkali perchlorates and permanganates, the author has examined the crystals deposited from a solution containing equal weights of potassium fluoborate and permanganate. Mixed crystals of the fluoborate type, containing at most 0·4% of the permanganate, are formed, but on the permanganate side the miscibility is practically zero.

T. H. P.

Crystalline Form of Trihydrated Sodium Chlorite. ETTORE ARTINI (*Atti R. Accad. Lincei*, 1922, [v], **31**, ii, 65—67).—This salt, $NaClO_2,3H_2O$ (cf. Levi, A., 1922, ii, 567), crystallises in the triclinic system: $a:b:c=0.4041:1:0.6353$, $\alpha=103°\ 43.5'$, $\beta=119°\ 3'$, and $\gamma=81°\ 46.5'$. T. H. P.

Purification of Sodium Hyposulphite: A Modification of Jellinek's Method. WALTER G. CHRISTIANSEN and ARTHUR J. NORTON (*J. Ind. Eng. Chem.*, 1922, **14**, 1126—1128).—An apparatus is described by means of which sodium hyposulphite of 98·3% purity can be rapidly obtained in 42% yield from the commercial article by a modification of Jellinek's procedure. It consists essentially of a source of carbon dioxide, connected, on the one hand, with a bottle cemented with litharge and glycerol into a Büchner filter, the bottom of the bottle being removed and replaced with canvas and hardened filter-paper, and, on the other, with a litre bottle, standing in a 2-litre beaker which serves as a water-bath, and provided with a combined stirring and filtering device. The latter consists of an inverted glass funnel sealed on to a glass tube which acts also as the shaft of the stirrer. The whole apparatus is exhausted and filled with carbon dioxide, the solution of commercial hyposulphite in freshly distilled water is introduced into the Buchner filter, and the clear yellow filtrate is passed by the gas pressure into an intermediate receiver and thence into the litre bottle previously charged with the requisite quantity of sodium chloride. The stirrer is set in motion for about thirty minutes to ensure complete solution of the salt and precipitation of the hydrated hyposulphite. The washing, dehydration, and drying of the precipitate is carried out as in Jellinek's method (A., 1911, ii, 278). The ferricyanide method was found superior to either the copper or silver methods for the estimation of the purity of the product. G. F. M.

Sodium Chromite. ERICH MÜLLER (*Z. angew. Chem.*, 1922, **35**, 557—558).—Chromium hydroxide was precipitated from a solution of a chromic salt by ammonia, dried over sulphuric acid, shaken with sodium hydroxide of different concentrations, and the concentration of chromium determined from time to time. The presence of hydroxide in solution begins to be noticeable with $5N$-sodium hydroxide solution. The hydroxide used contained about 6 mol. of water to 1 mol. of chromium trioxide. The amount of hydroxide dissolved was found to be dependent on the time the mixture was agitated, rising to a maximum and after this decreasing to an almost constant value. The minimum solubility set in after from ten to fourteen days. The chromium seems to exist in solution as a complex ion, and not as a colloid. It is considered that a tervalent chromium salt of sodium is formed. H. M.

Ammoniacal Silver Fluoride. DERVIN and OLMER (*Compt. rend.*, 1922, **175**, 1058—1061; cf. Gore, *Chem. News*, 1870, **21**, 28; Bruni and Levi, A., 1916, ii, 482, 617).—Anhydrous

silver fluoride dissolved in cold concentrated ammonia solution and the solution evaporated first in a vacuum, then at normal pressure over concentrated sulphuric acid, yielded colourless orthorhombic prisms having the composition $AgF,2NH_3,2H_2O$. Light slowly decomposes this substance, but it may be preserved unchanged in the dark. It is very soluble in water, the solubility increasing on addition of ammonia, and although the solubility in alcohol is increased by the presence of water, addition of alcohol to the aqueous solution does not result in precipitation. Dry ammonia gas is without action on the crystals; if placed in a vacuum over sulphuric acid, they lose water, and when the anhydrous state is reached loss of ammonia takes place. On being heated, ammoniacal silver fluoride detonates, the products including nitrogen, finely divided silver, and ammonium fluoride. The authors suggest that the decomposition may be represented by the equation $3(AgF,2NH_3,2H_2O) \longrightarrow Ag_3N+3NH_4F+2NH_3+6H_2O$, with subsequent breaking up of the silver nitride into its elements.

H. J. E.

The Dissociation of Calcium Sulphate at High Temperatures. P. P. Budnikov and J. K. Syrkin (*Chem. Ztg.*, 1923, **47**, 22).—Samples of calcium sulphate were heated to constant weight at temperatures of from 800° to 1375° and the proportion of calcium oxide in the product was determined in each case. After heating at 1000°, only 0·21% of calcium oxide was present, at 1300°, 3·00%, and at 1375°, 98·67%. Above 1300° the salt melts and a vigorous evolution of fumes takes place corresponding with almost complete decomposition.

A. R. P.

Valency. XIX. The Ammonia Compounds of Barium Halides. Gustav F. Hüttig and Wilhelm Martin (*Z. anorg. Chem.*, 1922, **125**, 269—280).—The following ammonia compounds were found to exist, $BaCl_2,8NH_3$; $BaBr_2,8NH_3$; $BaBr_2,4NH_3$; $BaBr_2,2NH_3$; $BaBr_2,NH_3$; $BaI_2,10NH_3$; $BaI_2,9NH_3$; $BaI_2,8NH_3$; $BaI_2,6NH_3$; $BaI_2,4NH_3$, and $BaI_2,2NH_3$. The method of investigation was the same as before (cf. A., 1920, ii, 293 and 318). The dissociation temperature at which the pressure equals 100 mm. is given in each case, and also the heat of formation as calculated by Nernst's formula.

W. T.

Complex Magnesium Salts. III. G. Spacu and R. Ripan (*Bulet. Societ. Ştiinţe Cluj*, 1922, **1**, 267—283; from *Chem. Zentr.*, 1922, iii, 1046—1047; cf. this vol., i, 96).—*Monoaquopentamminemagnesium chloride*, $[Mg(NH_3)_5,H_2O,]Cl_2$, prepared by passing ammonia into a solution of magnesium chloride in absolute alcohol at the ordinary temperature, is a colourless, crystalline powder. The following are also mentioned: *hexamminemagnesium bromide*, a white, crystalline powder; *tetra-aquodiamminemagnesium sulphate*, $[Mg(NH_3)_2(H_2O)_4]SO_4$, a crystalline powder; *triaquotriamminemagnesium sulphate*, $[Mg(NH_3)_3(H_2O)_3]SO_4$, colourless crystals; *diaquodiamminemagnesium sulphate*, $[Mg(NH_3)_2(H_2O)_2]SO_4$, white

powder; *triaquopiperidinemagnesium sulphate*,

$[Mg(C_5NH_{11})(H_2O)_3]SO_4$,

a slightly green substance; *penta-aquobenzylaminemagnesium sulphate*, a white, crystalline powder. G. W. R.

The Solidification of the System $MgCl_2$–KCl–$BaCl_2$. J. VALENTIN (*Compt. rend.*, 1922, **175**, 1061—1063).—A thermal study of the three salts was made and the results are shown in a series of diagrams. Two compounds, $MgCl_2$,KCl and $BaCl_2$,2KCl, are formed, so that the complete triangular diagram is divided into five regions, each corresponding with the deposition of a pure substance and contains three triple points. H. J. E.

A Simple Method for the Preparation of Highly Phosphorescent Zinc Sulphide. JULIUS SCHMIDT (*Ber.*, 1922, **55**, [*B*], 3988—3989).—Equal weights of pure zinc sulphate and sodium acetate are dissolved in water and the hot solution is treated with hydrogen sulphide until the precipitation of the zinc is complete. The zinc sulphide is washed by decantation and finally completely on the filter, after which it is dried on the water-bath. The product (200 g.) is moistened uniformly with a solution of magnesium chloride (20 g.), calcium chloride (10 g.), strontium chloride (10 g.), and crystalline barium chloride (10 g.) in water (200 c.c.) to which 0·04 g. of ammonium tungstate dissolved in 10 c.c. of water has been added. The mixture with the zinc sulphide is evaporated to dryness with occasional stirring on the water-bath. The product is slowly heated to redness in a crucible (the operation should require about an hour) and maintained at this temperature during thirty to forty minutes, after which it is allowed to cool in the furnace. The soluble salts are removed by water and the residual zinc sulphide is dried on the water-bath. It exhibits a strong, green fluorescence.

Mixtures of salts other than those described have little influence on the strength but considerable effect on the colour of the phosphorescent light and the readiness with which the phosphorescent effect is excited by illumination, Röntgen rays, or radioactive materials. Most metallic salts induce a green phosphorescence, but that caused by manganese is yellow (cf. Hofmann and Ducca, A., 1904, ii, 690). Phosphorescence appears to be weakened or completely inhibited by metallic salts, which give dark coloured or black sulphides (cf. MacDougall, Stewart, and Wright, T., 1917, **111**, 663). H. W.

Action of Natural Waters on Lead. JOHN C. THRESH (*Analyst*, 1922, **47**, 459—468, 500—505).—The presence of varying quantities of silicates, carbonates, sulphates, and salts of organic acids, together with the organic acid and free carbon dioxide, causes the differences observed in the action of natural waters on lead. Silicates prevent the oxidation of lead, iron, and aluminium, and moorland water after treatment with sodium silicate ceases to act on lead. W. P. S.

Complex Salts of Copper and Thallium. G. CANNERI (*Gazzetta*, 1922, **52**, ii, 266—270).—The following complex compounds, analogous to the simplest types of those of the alkali elements (cf. Rosenheim and Steinhäuser, A., 1900, ii, 653), are described: $Tl_2Cu(SO_4)_2,6H_2O$, blue crystals; $Tl_2Cu(SO_3)_2$, yellow powder; $CuSO_3,3Cu_2SO_3,Tl_2SO_3$, cinnabar-red crystals, dissolving in aqueous ammonia to a blue solution; $Tl_4Cu(S_2O_3)_3$, a straw-yellow, microcrystalline powder. No more than one compound corresponding with one and the same series was obtained, in spite of variation of the conditions of formation. T. H. P.

The Vapour Tension of some Copper–Zinc Alloys in the Solid State. LÉON GUILLET and MARCEL BALLAY (*Compt. rend.*, 1922, **175**, 1057—1058).—The rate of volatilisation of zinc from copper-zinc alloys depends on the temperature and on the nature of the surrounding atmosphere. When the latter can exhibit oxidising properties, the surface film of oxide mechanically retards loss of zinc from the alloy, whilst in an atmosphere of carbon monoxide, nitrogen, or hydrogen no film is formed and the temperature alone is the controlling factor. In such cases, the vapour pressures observed cannot be represented as a linear function of the atomic percentage of dissolved copper, as the alloys used ($Cu=55{\cdot}20\%$, $Zn=44{\cdot}75\%$) were not dilute solutions of copper in zinc. Raoult's law, therefore, does not hold. H. J. E.

Solubility of Halides of Univalent Copper in Sodium Thiosulphate. G. CANNERI and R. LUCHINI (*Gazzetta*, 1922, **52**, ii, 261—266).—In the compounds originating when cuprous halides are dissolved in ammonium thiosulphate solution, the univalent copper apparently exerts its co-ordinating power, not merely towards the thiosulphuric radicle, but also towards the halogen.

To the compounds formed, which have the general formula, $CuX,NH_4X,4(NH_4)_2S_2O_3$, where X represents a halogen atom or the thiocyanogen radicle (cf. Rosenheim and Steinhäuser, A., 1900, ii, 653), Werner ("Neuere Anschauungen," 1913, 168) ascribed the formula $\left[R\begin{smallmatrix}X_2\\(S_2O_3)_4\end{smallmatrix}\right](NH_4)_9$, R in this case representing Cu. On the basis of this formula, the integrity of the nucleus within the brackets should not be diminished by replacement of the ammonium residue by an atom of an alkali element of similar chemical character such as sodium. There seems, therefore, to be no reason sufficient to explain the difference in behaviour between the ammonium salts and those of other alkali metals other than the varying solvent power on the cuprous halides.

The authors find that sodium thiosulphate, fused in its own water of crystallisation, dissolves considerable proportions of freshly prepared cuprous halides and cuprous thiocyanate, the following salts being formed: $CuCl,5Na_2S_2O_3$; $CuBr,5Na_2S_2O_3$; $CuBr,Cu_2S_2O_3,9Na_2S_2O_3$; $CuBr,5Na_2S_2O_3,NaI$; $2CuCNS,5Na_2S_2O_3$.

To these compounds, which form white crystals unaffected by the action of light, and give clear, colourless, aqueous solutions,

the following formulæ, analogous to those attributed by Werner to the complexes formed by ammonium thiosulphate, might be ascribed: $\left[Cu\begin{smallmatrix}Cl\\(S_2O_3)_5\end{smallmatrix}\right]Na_{10}$; $\left[Cu\begin{smallmatrix}Br\\(S_2O_3)_5\end{smallmatrix}\right]Na_{10}$; $\left[Cu\begin{smallmatrix}Br\\(S_2O_3)_{10}\end{smallmatrix}\right]\begin{smallmatrix}Cu_2\\Na_{18}\end{smallmatrix}$; $\left[Cu\begin{smallmatrix}I\\(S_2O_3)_6\end{smallmatrix}\right]\begin{smallmatrix}Cu\\Na_{11}\end{smallmatrix}$; $\left[Cu\begin{smallmatrix}(CNS)_2\\(S_2O_3)_5\end{smallmatrix}\right]\begin{smallmatrix}Cu\\Na_{16}\end{smallmatrix}$.
Such hypothetical structural formulæ cannot, however, be supported by experimental data other than the colour of the salts, this indicating that the cuprous ion forms part of a complex radicle constituted of groupings in such condition that they exhibit increased resistance to react with their specific reagents. The dissociating action exerted by water on these complex compounds prevents physical measurements of any value in this connexion being made. T. H. P.

The Preparation of Metallic Phosphides by the Action of Hydrogen Phosphide on Solutions of Metallic Salts. A. Brukl (*Z. anorg. Chem.*, 1922, **125**, 252—256; cf. Moser and Brukl, A., 1922, ii, 393).—*Mercurous phosphide*, PHg_3, is obtained when hydrogen phosphide is allowed to react on a solution of mercurous sulphate in dilute sulphuric acid, as a black, amorphous precipitate; it is rapidly oxidised by the oxygen of the air, and gradually by dilute nitric acid. Phosphine is gradually evolved by the action of cold concentrated hydrochloric acid, but much more rapidly by the action of the hot acid; with concentrated sulphuric acid, sulphur dioxide is evolved. The compound is not explosive. Pure *mercuric phosphide*, P_2Hg_3, can be obtained by the action of a solution of mercuric chloride in ether on hydrogen phosphide; it is a dark brown solid, becoming grey on exposure to air. In the cold, water, alkalis, and dilute acids are without action, but on warming phosphine is evolved; it is oxidised in the cold by dilute nitric acid.

A solution of lead acetate in alcohol reacts with phosphine to form a black, flocculent precipitate of *lead phosphide*, P_2Pb_3, an unstable compound decomposed in the cold by water and alkalis.

Cadmium phosphide, P_2Cd_3, obtained as a black, flocculent precipitate by the action of phosphine on an ammoniacal solution of cadmium sulphate, is unstable, and yields hydrogen phosphide when treated with dilute hydrochloric acid. It is very vigorously oxidised by concentrated nitric acid. Its reactions are similar to those of lead phosphide. W. T.

Alloys of Iron and Aluminium. N. Kurnakov, G. Urasov, and A. Grigoriev (*Z. anorg. Chem.*, 1922, **125**, 207—227, and *J. Russ. Phys. Chem. Soc.*, 1918, **50**, 270).—The system iron–aluminium was studied by (1) thermal analysis, (2) the microstructure of the alloys, and (3) the electrical conductivity and hardness. In the interval 32·1—39·5 atom. % iron the endothermic compound, Al_3Fe_2, crystallises from the fused mass; below 1100°, this decomposes into the α- and β-solutions of aluminium in iron. Between 24·2 and 34 atom. % iron there exists a stable

phase, which the authors call the δ phase, having properties very different from those of the adjoining phases. This crystalline phase corresponds with the maximum change in properties of the system iron–aluminium; it possesses the minimum electrical conductivity and temperature coefficient, the maximum hardness, and it is extremely brittle. The authors regard it as a chemical individual of variable composition (cf. Kurnakov and Shemtschuschny, A., 1913, ii, 190). W. T.

Reducing Action of Ferrous Hydroxide. SUSUMU MIYAMOTO (*Japan J. Chem.*, 1922, **1**, 57—80, and *Sci. Papers Inst. Phys. Chem. Research*, 1922, **1**, 31—55).—An English translation of the paper previously published in Japanese (cf. A., 1922, ii, 647). The expression $K=e^{A-B/P}(1+0{\cdot}79C_{KOH})$ in the earlier paper should be replaced by $K=e^{A-B/T}(1+0{\cdot}79C_{KOH})$. K. K.

The Higher Oxide of Cobalt. OWEN RHYS HOWELL (T., 1923, **123**, 65—71).

Triple Nitrites of Bivalent Cobalt. V. CUTTICA and M. PAOLETTI (*Gazzetta*, 1922, **52**, ii, 279—286; cf. following abstract). —The analytical data given by Erdmann (*J. pr. Chem.*, 1866, **97**, 385) for the three triple nitrites, $Co(NO_2)_2,Ba[Ca,Sr](NO_2)_2,2KNO_2$, being incomplete, the authors have prepared and analysed these compounds, as well as various other triple nitrites of cobalt. The above three complex nitrites form dirty yellow powders stable in the air and may be regarded as salts of one and the same complex quadrivalent ion, $Co(NO_2)_6$. The latter is, however, not stable in presence of water, in contact with which the salts yield an insoluble golden-yellow compound, $K_2Co(NO_2)_4$, the stable cobaltonitrous ion being hence $[Co(NO_2)_4]''''$. The high value of the active mass of the ion $[NO_2]'$ present in the conditions of the reaction in which the triple salt originates tends to displace the equilibrium $[Co(NO_2)_4]''+2NO_2' \rightleftharpoons [Co(NO_2)_6]''''$ towards the right, a displacement in the same sense, that is, towards the formation of undissociated molecules of the triple nitrite, being determined also in the equilibrium $[Co(NO_2)_6]''''+2K^{\cdot}+Ca^{\cdot\cdot}$(or Ba,Ca) $\rightleftharpoons$ $\left[Co(NO_2)_6\right]\begin{matrix}K_2\\Ca\end{matrix}$. These cobalt compounds are analogous in composition to the corresponding nickel compounds, but exhibit greater stability towards the dissociating action of water, the co-ordination valency representing a far stronger linking in this case. If the potassium is displaced by thallium, a salt of analogous composition is obtained, but when sodium is introduced the composition is changed. Triple cobalt zinc (cadmium, mercury) potassium nitrites have also been obtained, these being stable in dry air and of the formula $\left[Co(NO_2)_6\right]_2\begin{matrix}Zn\\K_6\end{matrix}$.

The salts described and analysed are: cobalt calcium potassium nitrite; *cobalt barium thallium nitrite*; *cobalt barium sodium nitrite*, $Co(NO_2)_2,2Ba(NO_2)_2,NaNO_2$, a dirty green powder; *cobalt zinc potassium nitrite*, $2Co(NO_2)_2,Zn(NO_2)_2,6KNO_2$, dirty yellow; *cobalt*

cadmium potassium nitrite, pale chestnut, and *cobalt mercuric potassium nitrite*, rather deeper chestnut precipitate. T. H. P.

Triple Nitrites of Nickel. V. CUTTICA and G. CAROBBI (*Gazzetta*, 1922, **52**, ii, 270—279; cf. A., 1922, ii, 448).—Both the double and triple nitrites of nickel undergo profound ionic scission immediately on contact with water, the supposed ion, $[Ni(NO_2)_6]''''$, being hence classified with the "imperfect" complex ions. Hence in the passage of these salts into solution, the mobility of the constituent simple ions predominates over the co-ordinating action exerted in such conditions by the nickel. In general, accumulation of electronegative radicles in a complex ion is accompanied by increase in the extent of the ionic dissociation of its salts. With the complex nitrites, the large number of NO_2 radicles displaces the electrolytic equilibrium, $[Ni(NO_2)_6]K_4 \rightleftharpoons 4K^{\cdot}+[Ni(NO_2)_6]''''$, almost completely towards the right, and the equilibrium $[Ni(NO_2)_6]'''' \rightleftharpoons Ni(NO_2)_2+4NO_2'$ must also undergo displacement in the same sense. The results of cryoscopic measurements in water of some of the double and triple nitrites of nickel show, indeed, the almost exclusive presence of simple ions, the nickel nitrite molecules alone remaining undissociated. The following triple nitrites have been prepared.

Nickel mercuric potassium nitrite, $\left[Ni(NO_2)_6\right]^{K_2}_{Hg}$, forms dark green, almost black, crystals, and gives a green, aqueous solution. Cryoscopic measurements indicate decomposition into seven ions.

Two *nickel mercuric thallium nitrites* of the respective compositions: $3Ni(NO_2)_2,Hg(NO_2)_2,6TlNO_2$, orange-yellow crystals, and $2Ni(NO_2)_2,Hg(NO_2)_2,8TlNO_2$, are obtained according to the experimental conditions employed.

Nickel zinc potassium nitrite, $2[Ni(NO_2)_6]K_4,Zn(NO_2)_2$, forms a flesh-red, microcrystalline mass.

A chestnut-brown nickel uranyl thallium nitrite was prepared, but no simple formula could be derived from the results of its analysis.

Nickel cobalt potassium nitrite is a greenish-yellow salt of the formula

$$2K_4\left[Co(NO_2)_6\right]\left[Co(NO_2)_6\right]^{K_2}_{Ni} \text{ or } 2K_4\left[Co(NO_2)_6\right]\left[Ni(NO_2)_6\right]^{K_2}_{Co}.$$

Nickel cobalt thallium nitrite is a dark red salt which, when treated with water, leaves undissolved the orange-red complex, $Tl_2Co(NO_2)_4$. Its formula is probably $\left[Co(NO_2)_6\right]^{Tl_2}_{Ni},4TlNO_2$.

Unsuccessful attempts were made to prepare a nickel magnesium potassium nitrite. T. H. P.

Some New Series of Phosphotungstates. F. KEHRMANN and R. MELLET (*Helv. Chim. Acta*, 5, 942—944).—When a very concentrated solution of a mixture of sodium tungstate and phosphate is acidified faintly with acetic acid, at the end of a few days a mass of crystals separates containing two salts. One of these

can be freed from the other by washing with cold water, in which the first is sparingly soluble. This salt, which cannot be recrystallised, has the composition corresponding with the formula $14Na_2O,5P_2O_5,19WO_3$,aq or $29Na_2O,10P_2O_5,39WO_3$,aq. The second salt is readily soluble in cold water and forms supersaturated solutions which may not crystallise for months. The salt corresponds with the formula $3Na_2O,P_2O_5,6WO_3$,aq., representing the simplest series of phosphotungstates. A sodium salt described by Scheibler (*Ber.*, 1872, **5**, 801) was thought to belong to a $P_2O_5,6WO_3$ series, but is now shown to belong to the series $3M_2O,P_2O_5,7WO_3$,aq. It is proposed to continue the study of these three new series of phosphotungstates. E. H. R.

Properties of Tin, Especially the Density. R. Hoffmann and W. Stahl (*Metall. u. Erz.*, 1923, **20**, 5—8).—Tin of 99·8% purity produced from Bolivian ore at the Wilhelmsburg Works was found to have d_4^0 7·312 in a vacuum and d_4^{20} 7·311. [Cf. *J.S.C.I.*, 1923, Feb.] A. R. P.

The Equilibrium in the Reduction of Tin Dioxide by Carbon Monoxide. W. Fraenkel and K. Snipischski (*Z. anorg. Chem.*, 1922, **125**, 235—252).—The equilibrium $SnO_2+2CO \rightleftharpoons Sn+2CO_2$ was studied. It was found that the same equilibrium was reached from both sides, and it was independent of the amount and composition of the solid phases. The equilibrium concentration of carbon monoxide increases gradually with increasing temperature up to 900°, and then suddenly increases very rapidly. The temperature coefficient was studied; at 500°, equilibrium sets in after some weeks, whereas at 600° equilibrium is reached in a few days.

An improved method for the preparation of stannous oxide consists in dissolving stannous chloride in the least amount of hot concentrated hydrochloric acid, and gradually adding sodium hydroxide solution until the solution reacts alkaline towards phenolphthalein; the resulting milky liquid is then kept boiling in a bath of saturated sodium chloride solution. In a few hours a blue, lustrous powder is obtained; this is then washed and dried. W. T.

Composition of Micellæ. I. Stannic Acid Peptised by Alkali. Robert Wintgren (*Z. physikal. Chem.*, 1922, **103**, 238—259).—Electrical conductivity and transport measurements have been carried out with stannic acid sols which have been peptised by alkali and also with the filtrates from these obtained by ultrafiltration. From these measurements by Ducleaux's method (A., 1905, ii, 432), the portion of the conductivity and of the transport which is due to the micellar portion of the sol has been calculated, and from Zsigmondy's conception of the qualitative composition of the micellæ an attempt has been made to apply Kohlrausch's law of the independent migration of ions to inorganic colloid ions by regarding the micellar ions as ordinary multivalent ions. From the conductivity values the mean quantitative com-

position of the micella equivalent has been approximately determined, that is, the number of molecules of stannic oxide contained in one equivalent of colloidal stannic acid. This quantity has been termed the equivalent aggregation. Further, from the conductivity determinations it is shown, in agreement with Varga's calculations from transport measurements (*Kolloid Chem. Beihefte*, 1919, **11**, 25), that a measurable large quantity of the alkali used for peptisation is enclosed in the micellæ. The amount of enclosed alkali and the equivalent aggregation may be obtained indirectly from the transport measurements, and the quantities so obtained agree within a very little with those obtained from conductivity measurements and with those obtained by Varga. That considerable quantities of alkali are enclosed is shown by the fact that at the cathode, instead of an increase in alkali concentration occurring, a decrease is actually found. From the decrease in alkali concentration the amount enclosed can also be calculated and the quantity so obtained agrees well with the quantity obtained by the other methods. With increasing alkali content the equivalent aggregation decreases, as also does the percentage of enclosed alkali. On account of the small value of the conductivity of the sols with small alkali content, the composition can only be regarded as correct in respect of its order, and not as to its actual value. An example of the composition of a stannic acid sol examined is expressed as follows:

$$\left(1865SnO_2;\ 8{\cdot}83K_2O;\ xH_2O\,SnO_3H'\right)_n+nK^{\cdot}.$$

J. F. S.

Magnetic Analysis of the Stannic Acids. PAUL PASCAL (*Compt. rend.*, 1922, **175**, 1063—1065; cf. this vol., ii, 25).—The theoretical values of the molecular magnetic susceptibilities of the acids $Sn(OH)_4$ and $SnO(OH)_2$, calculated from those of stannates, methylstannonic acid, and metallic tin were compared with those obtained experimentally from stannic acids prepared by various methods. The results indicate that the acids are not definite compounds, but mixtures of anhydrous stannic oxide with water. H. J. E.

Zirkite Ore. J. G. THOMPSON (*J. Physical Chem.*, 1922, **26**, 812—832).—The mineral zirkite, an impure zirconium dioxide containing silica, iron, and titanium, has been investigated with the object of making it suitable for use as a refractory. It is shown that 90—95% of the silicon may be removed from the mineral by heating a mixture of the ore and carbon to a temperature above 2220° in an electric furnace. The best results are obtained by heating a mixture of the ore and coke in an arc furnace, the amount of carbon being approximately that required to transform only the silicon into carbide. If carbon in excess of this amount is used the separation of silicon is less complete, due to the formation of stable double carbides of silicon and zirconium. It is suggested that if the above treatment is followed by the removal of iron by treatment with chlorine a product, impure

zirconia, is obtained which is sufficiently refractory for most purposes. Zirconium carbide is shown to be exceedingly refractory, and infusible in a 40—50 kw. arc, but its use as a refractory is restricted, because it is necessary to protect it from oxidation. The various methods of analysis of zirconium compounds are discussed and a method for the estimation of zirconium, silicon, titanium, and iron in zirkite is outlined. J. F. S.

The Missing Element of Atomic Number 72. D. COSTER and G. HEVESY (*Nature*, 1923, **111**, 79).—From theoretical considerations, it is probable that the element of atomic number 72 is not a rare-earth metal, but a homologue of zirconium. Further, the conclusions of Dauvillier (A., 1922, ii, 463) and of Urbain (A., 1911, ii, 115) are considered not to be justified, since it appears that the quantity of the element in the sample examined by the former by an *X*-ray spectroscopic method must have been so small that its identity with the element claimed to have been detected by the latter in the same sample by optical and magnetic examination is improbable. The only lines, $L\alpha_1$ and $L\beta_2$, detected by Dauvillier were extremely faint, and the wave-lengths given are about 4X.u. (1X.u.$=10^{-11}$ cm.) smaller than those obtained by a rational interpolation in the wave-length tables of Hjalmar and Coster for the elements in the neighbourhood of atomic number 72. The authors have, however, by investigation of the *X*-ray spectrum of extractions of zirconium minerals, detected the lines $L\alpha_1=1565{\cdot}5$, $\alpha_2=1576$, $\beta_1=1371{\cdot}4$, $\beta_2=1323{\cdot}7$, $\beta_3=1350{\cdot}2$, $\gamma_1=1177$ X.u., which must be ascribed to the element of atomic number 72. The $L\alpha$ and $L\beta$ lines exactly agree with the anticipated mutual distance and relative intensity, and the wave-lengths all agree within one X.u. with those obtained by interpolation. A sample of a Norwegian zirconium mineral was estimated to contain at least 1% of the new element, whilst ordinary zirconium probably contains 0·01—0·1%. Experiments are in progress to isolate the new element, for which the name "hafnium" is proposed, and to determine its chemical properties. [Cf. Scott, T., 1923, 123, 311.] A. A. E.

The Anode Oxidation of Gold. FR. JIRSA and OT. BURYÁNEK (*Chem. Listy*, **16**, 299—305; cf. A., 1922, ii, 713).—A strong current was passed through a cell having a gold anode, and dilute sulphuric acid as electrolyte. After twenty-four hours the current was stopped, and the back *E.M.F.* of the anode measured. For the cell $Au|Au_2O_3,NH_2SO_4|NH_2SO_4,H_2|Pt$ this was $+1{\cdot}24$ volts at 18°. The same voltage was obtained whether the anode was prepared in the dark, or in the light of a mercury-vapour lamp, and reduction of the strength of acid from normal to $N/1000$ made no difference to this result. The rates of polarisation of gold anodes, using currents of 0·02 and of 0·5 milliampere/cm.^{2} were next measured, and the results shown on a graph. It was noticed that, below 0·02 milliampere, the results obtained were untrustworthy, owing to the slow rate of oxidation producing passivity in the gold. The rate of discharge of polarised gold anodes was

measured, under various conditions, and with the introduction of different resistances, in order to retard the rapidity of discharge. Gold anodes were next depolarised by passing currents of increasing magnitude through the cathode, until the polarisation *E.M.F.* disappears. The magnitudes of the polarisation currents produced by stationary and rotating oxidised gold anodes, using acids of different concentrations, were measured, and curves drawn showing the relation between the galvanometer readings and the voltage.

R. T.

The Occlusion of Hydrogen by Palladium. Mituo Yamada (*Phil. Mag.*, 1923, [vi], **45**, 241—243).—The crystalline structure of palladium, containing large quantities of absorbed hydrogen, has been determined by *X*-ray analysis. Except for slight contractions of the intervals between the lines on the röntgenogram, there is practically no difference between the figures for pure palladium and for this metal containing occluded hydrogen. The slight contraction corresponds with a uniform expansion of the space lattice. No new lines were observed, and hence a compound is not formed between the hydrogen and the palladium. The results are in accord with the view that the hydrogen is adsorbed in the state of solid solution. The expansion of the lattice determined from the displacement of the lines was 2·8%, which is in good agreement with the expansion, 2·9%, obtained by direct measurement.

W. E. G.

Mineralogical Chemistry.

Riebeckite from Vallone delle Minière (Valle della Germanasca). E. Grill (*Atti R. Accad. Lincei*, 1922, [v], **31**, ii, 137—142).—Black crystals of riebeckite, up to 7 mm. in length and with submetallic lustre and pronounced prismatic habit, were found on the eastern slope of Vallone delle Minière (Piedmont). They exhibit pleochroism and have *d* 3·44; the angle (100) : (110 is 55° 5′—55° 20′. Analysis gives :

SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	CaO	MgO	Na_2O	K_2O	H_2O-	H_2O+	Total
51·53	trace	2·71	16·22	17·11	0·22	0·79	1·01	7·81	1·13	0·31	1·20	100·04.

These results are in accord with the empirical formula :

$$13SiO_2,2(Fe,Al)_2O_3,4(Fe,Mg,Ca,Mn)O,3(Na,K,H)_2O.$$

T. H. P.

Analytical Chemistry.

Practical Spectroscopic Analysis. W. F. Meggers, C. C. Kiess, and F. J. Stimson (*Bull. Bur. Standards*, 1922, **18**, 235—255; *Sci. Paper*, No. 444).—A method of quantitative analysis is developed based on a study of the raies ultimes, and sensitive

lines which appear in the spectra of certain alloys. The raies ultimes are the most sensitive spectral lines of an element, and represent vanishing traces of its presence in a mixture or alloy. The most sensitive rays for eighty-three of the elements have been collected in one table by Gramont (A., 1922, ii, 73). In the present method of spectrographic analysis, use is made of standard samples, synthetic alloys, or salts mixed in definite proportions. The spectra of several standard samples are photographed alongside the spectrum of the unknown material, and the quantitative determination becomes a process of simple comparison. The condensed spark with self-induction in the spark circuit has been found to yield the best results. Three examples of the application of the method are illustrated, dealing with the determination of impurities in samples of tin, gold, and platinum. Many of the lines were sensitive for less than 0·001% of impurity. Other applications of spectrographic analysis are discussed. W. E. G.

A Colorimeter for Bicolorimetric Work. VICTOR C. MYERS (*J. Biol. Chem.*, 1922, **54**, 675—682).—A colorimeter of the Hellige type is described which contains three wedge-shaped vessels for the standards. Only one wedge is necessary for ordinary colorimetric work. For colorimetric estimations of hydrogen-ion concentrations, however, two wedges are employed, one containing a standard on the alkaline side, the other one on the acid side of the unknown. Using these in conjunction, a match can be obtained without the preparation of further standards. If the unknown solution is slightly turbid or coloured, the third wedge may be brought into use. E. S.

Chromoscope for the Measurement of the Concentration of Hydrogen-ions in Liquids by means of Coloured Indicators. CH. O. GUILLAUMIN (*J. Pharm. Chim.*, 1922, [vii], **26**, 452—454).—The apparatus consists essentially of a wooden box having six holes in two rows into which the tubes containing the solutions fit. Observations are made through lateral openings in a line with the axis of each row of tubes. The openings are shielded from external diffused light by means of a hood. The illumination of the tubes is effected either by diffused daylight or by artificial light, and either directly, or by reflection from an opal plate with a matt surface fixed at an angle of 45° to the plane of the observation tubes. A light filter is provided to correct, where necessary, for the dichroism of certain indicators. G. F. M.

Electrical Determination of the End-point of a Titration. ERICH MÜLLER (*Z. angew. Chem.*, 1922, **35**, 563—566).—The electrical potential of the reaction may serve as an indicator of the end-point of a titration, in so far as it is a question of the reaction of ions. An electrode has to be selected to correspond with one stage of the reaction, for example, in the titration of an iodide with silver nitrate, an electrode of silver, and an indifferent electrode of platinum. The potential of the reaction $\epsilon = A_1 + 0{\cdot}058_{\log c_{Ag}} = A_2 - 0{\cdot}058_{\log c_I}$. At the end-point $c_{Ag} = c_I$, and the

potential of this end-point may be determined by saturating water with silver iodide, acidifying with sulphuric acid, and immersing a silver electrode. This end-point electrode is connected through a galvanometer capable of indicating 10^{-5} to 10^{-7} amperes with the indicator silver electrode of a titration; the end-point of the titration is indicated by the needle reaching zero. H. M.

Quantitative Analysis by Measurement of the Degree of Supersaturation. HANS RÖDER (*Chem. Ztg.*, 1922, **46**, 1089).—A number of factors, such as the physical condition of the precipitate formed, the presence of substances which affect the solubility of the precipitate or hinder its formation, etc., must be taken into account in the method proposed by Höppler (A., 1922, ii, 863), and although the method is useful in certain cases much investigation is required before it is capable of wider application. W. P. S.

Contamination of Water Samples with Material Dissolved from Glass Containers. W. D. COLLINS and H. B. RIFFENBURG (*J. Ind. Eng. Chem.*, 1923, **15**, 48—49).—Samples of water in good glass bottles will not dissolve enough glass in a month to cause any detectable change in the ordinary mineral analysis, and even in six months no significant change will be caused. In bad bottles, sufficient mineral matter may be dissolved in a day, and certainly in a week, to change the character of the water. The greatest changes are an increase in silica and sodium, and a change of the alkalinity from bicarbonate to carbonate and hydroxide with an increase in total alkalinity corresponding with the sodium dissolved. Bottles may be tested for resistance to solution by filling with distilled water and examining after a month. Titration with acid and estimation of the total solids and the silica will show the extent of the action. G. F. M.

Alumina as an Absorbent for Water in Organic Combustions. H. L. FISHER, H. L. FAUST, and G. H. WALDEN (*J. Ind. Eng. Chem.*, 1922, **14**, 1138—1139).—The preparation of alumina for use in absorbing water in organic combustions is described. It may be made either from the hydroxide or from the hydrated chloride. In the first case, the hydroxide is first mixed with 20% of purified and ignited asbestos and then ignited over a bunsen flame. In the second case, pumice is saturated with a solution of aluminium chloride, the whole evaporated to dryness with stirring, and ignited at 700—750° until no more hydrogen chloride is given off. The advantages of alumina over other absorption agents are that, being a solid, it offers less resistance to the passage of gases than sulphuric acid, does not form crystalline hydrates like calcium chloride, or contain basic substances which absorb carbon dioxide, and does not clog the apparatus like phosphoric oxide. H. C. R.

Some Sources of Error in the Estimation of Chlorides in Blood and Similar Material. ISIDOR GREENWALD and JOSEPH GROSS (*J. Biol. Chem.*, 1922, **54**, 589—594).—The results obtained

in the estimation of chlorides in whole blood differ according to the particular protein precipitant used. Using as a standard for comparison the results obtained by the oxidation of blood with nitric acid in the presence of silver nitrate, the authors find that tungstic acid is the most suitable precipitant. Picric acid leads to high results owing to the formation of purine-silver picrates, whilst other precipitants cause either low or irregular results.

E. S.

Detection, Elimination, and Estimation of Ammonia in Hydroxylamine Hydrochloride. RAOUL GROS (*J. Pharm. Chim.*, 1922, [vii], **26**, 449—452).—For the detection of ammonia, the hydroxylamine in the sample is first destroyed by the addition of a solution of iodine and of potassium hydrogen carbonate or sodium acetate, the excess of iodine being finally eliminated by means of thiosulphate. The liquid thus treated is then tested for ammonia by means of Nessler's solution, or by warming with alkali hydroxide, or by means of sodium hypobromite.

Ammonia may be eliminated from hydroxylamine salts by taking advantage of the volatility of ammonium hydrogen carbonate. The solution of the salt, to which a sufficient quantity of potassium hydrogen carbonate has been added, is warmed in a flask on a water-bath, and air is drawn through by means of a water pump.

The estimation of the ammonia is effected by interposing a flask containing standard sulphuric acid between the flask containing the hydroxylamine solution and the pump. All the ammonia will have been volatilised and absorbed in the acid in about one hour, and the excess of acid is then titrated with alkali. In one instance, ammonia equivalent to 31% of ammonium chloride was found in a reputedly pure specimen of hydroxylamine hydrochloride.

G. F. M.

The Nitrometer Method for the Estimation of Nitrogen in Nitrates and Nitric Acid. H. W. WEBB and M. TAYLOR (*J. Soc. Chem. Ind.*, 1922, **41**, 362—364T).—Nitrogen in potassium nitrate can be correctly estimated by means of the nitrometer if 91—92% sulphuric acid is employed, and a correction of 0·2 c.c. per 10 c.c. of acid used is applied for the solubility of nitric oxide in the acid. The correction for the solubility of nitric oxide in sulphuric acid given by Lunge (0·35 c.c. in 10 c.c. acid) is too high. Nitric acid can also be estimated to within $\pm$0·15% if it is weighed out in such a way as to avoid loss of fume by weighing out a large quantity into a known weight of sulphuric acid contained in a deep bottle, and then weighing out the necessary amount of the mixed acid into the nitrometer. The estimations should be conducted in a room free from rapid fluctuations in temperature, and the latter should be read before the volume of gas in each case.

G. F. M.

The Absorption and Analysis of Gaseous Oxides of Nitrogen. A. SANFOURCHE (*Bull. Soc. chim.*, 1922, [iv], **31**, 1248—1264).—Determinations of the rate of absorption of nitric oxide, and of

the products of the oxidation of this gas, by sulphuric acid and mixtures of sulphuric and nitric acid, show that the mechanism of absorption is very different in the two cases. Nitrous gases having a composition represented approximately by the formula N_2O_3 were absorbed with much greater rapidity than either pure nitrogen dioxide or peroxide, and the theory that the trioxide reacts as a mixture of the other two is therefore untenable. On the contrary, it is nitrogen trioxide which reacts with the sulphuric acid, and is continuously regenerated from its dissociation products according to the reversible equation $N_2O_3 \rightleftharpoons NO+NO_2$. Absorption by alkalis occurs in the same way, and the contention of Lunge that the peroxide initially reacts giving equimolecular proportions of nitrate and nitrite and that the former is then reduced to nitrite by the dioxide is inadmissible. The use of alkaline liquids as absorbents for nitrous gases in analysis, however, always gives a larger proportion of nitrogen in a higher state of oxidation than when sulphuric acid is used as absorbent. This is due to secondary reactions with the water, or water vapour, and is always more pronounced when the alkali hydroxide is only in slight excess. Nitrous acid is momentarily formed and decomposes into nitric acid and nitric oxide; the latter is either unabsorbed, or else in presence of oxygen again passes through the cycle of changes, the net result of which is to increase the nitrate at the expense of the nitrite. These errors can only be avoided by securing complete absorption on first contact of the gases with the alkaline solution by using a large excess of alkali and stirring the solution vigorously. This is not always possible, and hence absorption by sulphuric acid is considered preferable. G. F. M.

Estimation of Phosphorus. G. E. F. LUNDELL and J. I HOFFMAN (*J. Ind. Eng. Chem.*, 1923, **15**, 44—47).—The sources of error in the precipitation of phosphorus as ammonium phosphomolybdate and its subsequent estimation by weighing as ammonium pyrophosphate or by titration with alkali, and the precautions necessary to guard against them are described in detail, with special reference to the estimation of small amounts of phosphorus in metallurgical products. The precipitation of the phosphomolybdate should be carried out at 40—60° in a solution containing 5—10% of nitric acid, 5—15% of ammonium nitrate, and a 15—25-fold excess of ammonium molybdate, and the precipitate should be kept with frequent shaking for at least forty minutes for a technical analysis, or over-night where great accuracy is required. The phosphorus must all be present initially as orthophosphate. The precipitate must be washed with 1—2% nitric acid, excessive washing being avoided. Fluorine, quinquevalent vanadium, titanium, zirconium, arsenic, and silicon contaminate the precipitate and delay precipitation, and absolutely correct estimations of phosphorus can only be obtained by dissolving the precipitate, and reprecipitating the phosphorus as a pure compound of definite composition, such as magnesium ammonium phosphate. On dissolving the precipitate in dilute ammonia, as

is usual, a small, insoluble residue of the phosphates of iron, titanium, zirconium, and tin will remain if these elements are present. This may sometimes be dissolved by adding citric acid to the ammoniacal solvent, otherwise the filter-paper and the precipitate must be fused with alkali, and extracted with water, adding the extract to the ammoniacal solution. Magnesium ammonium phosphate is precipitated from this solution by rendering slightly acid with hydrochloric acid, adding 0·2—0·5 g. of citric acid, a 5—10-fold excess of magnesia mixture, and ammonia to slight alkalinity. In presence of the above-mentioned elements, the precipitation must be repeated. If contamination by arsenic is feared, it must be removed at this stage by precipitation with hydrogen sulphide. For routine analysis of small amounts of phosphorus in iron, steel, bronze, etc., titration of the phosphomolybdate precipitated under standard conditions is quite satisfactory. The precipitate is first washed with cold 1—2% nitric acid, followed by 1% neutral potassium nitrate solution. It is then dissolved in excess of standard alkali, and the excess titrated back with standard acid, with phenolphthalein as indicator. The phosphorus equivalent of the alkali must be determined by analysis of a pure phosphate under the standard conditions. A fifteen-minute precipitation is sufficient for alkalimetric estimations except in abnormal conditions, such as when vanadium or much hydrochloric acid is present, when at least thirty minutes should be allowed before filtering. In presence of arsenic, the tendency is towards high values. G. F. M.

The Iodometric Estimation of Arsenic Acid. I. M. Kolthoff (*Z. anal. Chem.*, 1923, **62**, 137—138).—In the determination of arsenic acid by titration of the iodine liberated by addition of potassium iodide to the hydrochloric acid solution, all danger of obtaining high results by atmospheric oxidation may be obviated by warming the solution of arsenic acid with an equal volume of *N*-hydrochloric acid on the water-bath for five minutes, then adding potassium iodide to a concentration of 25%, closing the flask, warming for a further five to ten minutes, cooling, and titrating with thiosulphate. The result may be checked by neutralising the titrated liquor with sodium hydrogen carbonate and titrating with iodine. Slightly high results are obtained in the first process if the iodide is added before warming the acidified solution. (Cf. Rosenthaler, A., 1922, ii, 584; Fleury, A., 1920, ii, 448; Kolthoff, A., 1921, ii, 463.) A. R. P.

Estimation of Carbon Dioxide in Dilute Concentration. Keiichi Shikata and Shigeru Saruhashi (*J. Pharm. Soc. Japan*, 1922, No. 488, 893—907).—An improvement of the method of estimating carbon dioxide by the decrease of the volume of a potassium hydroxide solution which absorbs it. For the purpose, the authors have constructed an apparatus consisting of a sensitive differential manometer and a graduated capillary (2 c.c. volume and 38 mm. length) attached to a balloon of 198 c.c. capacity. With the

apparatus as little as 0·004% of carbon dioxide can be estimated accurately. K. K.

Gasometric Method for the Estimation of Carbon Dioxide in Carbonates. C. TUBANDT and HARRY WEISZ (*Chem. Ztg.*, 1922, **46**, 1105).—The carbonate is placed in a small reaction vessel which is attached to the lower end of a small vertical condenser, an acid chamber being fitted between the end of the condenser and the reaction vessel. Taps are provided between the acid chamber and the reaction vessel and at the top of the condenser. A tube connects the top of the condenser with a gas-measuring burette. The latter is provided with a water-jacket, and this is connected with the jacket of the condenser and with a bath surrounding the reaction vessel, so that the whole apparatus may be brought to the same temperature. After the acid has been admitted to the reaction vessel and the greater part of the carbon dioxide has been collected in the burette, the water in the vessel surrounding the reaction vessel is boiled for a short time, then cooled rapidly, and after the temperature of the whole apparatus has been brought to that at which it was originally, the volume of the gas is measured. W. P. S.

Estimation of the Titratable Alkali of the Blood. ISIDOR GREENWALD and GERTRUDE LEWMAN (*J. Biol. Chem.*, 1922, **54**, 263—283).—The method is designed for clinical use. Oxalated blood is precipitated with picric acid. Estimations are then made of (1) free picric acid, and (2) total picric acid in the filtrate, the difference representing the alkali previously combined with protein or carbonic acid in the blood. Free picric acid is estimated by direct titration with sodium hydroxide in the presence of a suitable indicator, and total picric acid either gravimetrically as nitron picrate or volumetrically, using titanous chloride. E. S.

Analysis of Sodium Perborate. HERMANN BURKARDT (*Chem. Ztg.*, 1923, **47**, 6).—The available oxygen content of the salt is determined by titration of the solution acidified with sulphuric acid with $N/4$-potassium permanganate. A second quantity of 2·5 g. is dissolved in water and the solution is titrated with $N/2$-hydrochloric acid, using methyl-orange as indicator. After boiling under a reflux condenser for five minutes, the solution is cooled, treated with 10 c.c. of neutral glycerol and a few drops of phenolphthalein, and titrated against $N/2$-sodium hydroxide to a pale pink colour. If, after addition of more glycerol the colour disappears, more alkali and glycerol are added until the pink colour persists. From these three results the percentages of borate and perborate present may be calculated. A. R. P.

Estimation of Calcium in the Blood. GIOVANNI DE TONI (*Arch. Farm. sperim. Sci. aff.*, 1922, **34**, 124—128, 129—130, 145—149).—The author finds that Jansen's method for estimating calcium in the blood (A., 1918, ii, 174) gives results of satisfactory accuracy, provided that the mean of two or three separate estimations is taken; the amount, 10 c.c., of blood required for each

estimation is unduly large, especially in the case of an infant. Marriott and Howland's method (A., 1918, ii, 21) is untrustworthy.

T. H. P.

The Application of Conductometric Methods to Precipitation Analysis. VI. Conductometric Titrations with Lithium Sulphate. I. M. KOLTHOFF (*Z. anal. Chem.*, 1923, **62**, 1—7).—Barium salts even in very dilute solution may be accurately titrated conductometrically by means of lithium sulphate solution if about 30% of alcohol is added to the liquid. In the presence of calcium, high results are obtained, probably due to co-precipitation of calcium sulphate. Calcium and strontium salts cannot be titrated in the above manner, but lead salts in greater dilution than 0·01 mol. give excellent results, although more concentrated solutions yield results as much as 4% too low. A. R. P.

The Application of Conductometric Methods to Precipitation Analysis. VII. Conductometric Titrations with Sodium Chromate. I. M. KOLTHOFF (*Z. anal. Chem.*, 1923, **62**, 97—103).—Barium, lead, and silver in neutral solutions may be accurately estimated by conductometric titration with sodium chromate. In acid solutions, only lead gives good results, the other two metals forming dichromates. Strontium salts interfere with the barium estimation. Alone, strontium may be titrated in a similar way to barium, provided 50% of alcohol is added to the solution, but manganese, zinc, copper, and cadmium cannot be satisfactorily titrated in this manner, as they all form more or less basic salts none of which is of constant composition. By addition of an excess of potassium dichromate to a neutral solution of a lead salt of a strong acid and subsequent titration conductometrically of the liberated chromic acid with standard alkali (to dichromate), accurate results are obtained, as the first dissociation constant of chromic acid is so large whilst the second is exceedingly small.

A. R. P.

Colorimetric Method for the Estimation of Small Amounts of Magnesium. F. S. HAMMETT and E. T. ADAMS (*J. Biol. Chem.*, 1922, **54**, 565—566).—In the authors' method (A., 1922, ii, 587), separation of the ammonium magnesium phosphate by centrifuging is preferable to filtration through a Gooch crucible owing to the presence of small quantities of phosphorus in the asbestos used in the crucible. E. S.

The Estimation of Magnesium in Aluminium Alloys. W. H. WITHEY (*Chem. News*, 1923, **126**, 17—19).—Two g. of the alloy are dissolved in aqua regia and the solution is evaporated with sulphuric acid until the latter fumes strongly. After cooling and diluting, the silica is filtered off and the filtrate treated with 15 g. of tartaric acid, 5 g. of ammonium chloride, ammonia until distinctly alkaline, 25 c.c. of saturated sodium phosphate solution, and a further quantity of strong ammonia equal to one-third the bulk of the solution. After stirring and remaining over-night, the precipitate is collected, washed, ignited, and weighed as magnesium

pyrophosphate in the usual way. If the alloy contains manganese, the precipitate will be contaminated with this element, the amount of which must be estimated by the bismuthate method and the corresponding weight of manganese pyrophosphate deducted. Copper, nickel, zinc, aluminium, and iron do not interfere.

A. R. P.

A New Method of Estimating Magnesium in Aluminium Alloys. Buntarô Otani (*J. Chem. Ind. Japan*, 1922, **25**, 1305—1310).—The method depends on the fact that magnesium is precipitated as phosphate by means of sodium phosphate in the presence of tartaric acid (equivalent to 1·5 times the aluminium in the solution), whilst the aluminium remains in the solution as a soluble salt: $Al(OH)_3+C_4H_6O_6 \longrightarrow C_4H_4O_6Al\cdot OH+2H_2O$. For precipitation of the magnesium phosphate the mixture must be left for six hours, but the time must be increased if the magnesium is present in very small amount. K. K.

Estimation of Zinc as Zinc Ammonium Phosphate and its Application in the Separation of Zinc from other Metals. II. P. Artmann (*Z. anal. Chem.*, 1923, **62**, 8—17; cf. A., 1915, ii, 181).—The influence of ammonium nitrate, chloride, tartrate, and acetate and of the corresponding acids on the precipitation of zinc ammonium phosphate has been investigated, and the following conditions are recommended for obtaining the best results. The warm ammoniacal solution (60—70°) containing ammonium-ions in a concentration not exceeding $N/1$ is neutralised with nitric acid and treated with six times the theoretical quantity of ammonium phosphate solution; the minimum amount of the latter, however, should be sufficient to render the solution after precipitation at least $N/5$ in respect to this reagent, *i.e.*, 10 c.c. of $3N$-ammonium phosphate solution per 150 c.c. If ammonium tartrate is also added, as in the case of separation of zinc from other elements, a further 3 c.c. of the phosphate solution must be used for every 10 c.c. of $2N$-ammonium tartrate solution added. Prolonged heating after precipitation must be avoided, as it tends to convert the zinc ammonium phosphate into tertiary zinc phosphate; to obtain an easily filterable precipitate the solution should be heated just to boiling with continuous stirring and then left for twenty minutes on the water-bath. A. R. P.

Estimation of Zinc as Zinc Ammonium Phosphate and its Application to the Separation of Zinc from other Metals. III. Separation of Zinc from Mercury and Nickel. P. Artmann and Walter Hartmann (*Z. anal. Chem.*, 1923, **62**, 17—23).—For the separation of zinc from mercury, the faintly acid solution of the mixed nitrates containing less than 0·1 g. of zinc and 0·4 g. of mercury is treated with 6 g. of ammonium nitrate and made just ammoniacal. Ten c.c. of $3N$-ammonium phosphate solution are added, and the mixture is heated at 60°, neutralised with $5N$-nitric acid, heated to boiling, and left for thirty minutes on the water-bath. The precipitate is washed by decantation first with

hot 1% ammonium phosphate solution, then with cold water, dried at 105°, and weighed as zinc ammonium phosphate. If more mercury than zinc is present, the precipitate is dissolved in nitric acid and the zinc reprecipitated as before.

The separation of zinc from nickel is carried out in a similar manner, except that the ammonium nitrate is replaced by 30 c.c. of 2*N*-ammonium tartrate solution and 1—2 g. of sodium acetate are added before neutralisation. Double precipitation is necessary in all cases. A. R. P.

The Electrometric Estimation of Zinc and Lead in the same Solution by Means of Potassium Ferrocyanide. ERICH MÜLLER and KURT GÄBLER (*Z. anal. Chem.*, 1923, **62**, 29—34).—Zinc and lead may be titrated consecutively by the addition of a 0·1 mol. solution of potassium ferrocyanide to a neutral solution of the two metals containing 1 c.c. of a 0·1 mol. solution of potassium ferricyanide per 100 c.c., the end-points being determined conductometrically. The first knick in the curve corresponds with the complete precipitation of zinc as $K_2Zn_3[Fe(CN)_6]_2$, and the second to that of lead as $Pb_2Fe(CN)_6$. The titration is carried out at 75°, and a platinum gauze is used as indicator electrode. This is connected through an electrolytic switch filled with saturated potassium nitrate solution to the normal calomel electrode and the potential difference between the indicator and normal electrodes is measured by means of a Poggendorff capillary electrometer. In order to obtain accurate results by this method, the solution must be left for several minutes after each addition of reagent when the zinc end-point is being approached. An alternative procedure consists in dividing the solution into two equal parts and determining the sum of the zinc and lead in one part and the zinc alone, after addition of sufficient sulphuric acid just to precipitate the lead, in the second part. Both titrations are carried out at 75°, the former with an applied potential of +0·19 volt and the latter with +0·50 volt. The presence of excessive quantities of nitrates or acetates interferes with the lead titration. A. R. P.

Gravimetric Analysis. XXVII. Estimation of Lead. II. L. W. WINKLER (*Z. angew. Chem.*, 1922, **35**, 715—716).—In the presence of iron, the method described in the previous paper (this vol., ii, 40) is inapplicable. Good results are, however, obtained if the lead and ferric nitrate solution containing 1 c.c. of *N*-nitric acid in 100 c.c. are treated in the cold with 10 c.c. of a cold 10% ammonium sulphate solution. After remaining over-night, the precipitate is filtered on a Gooch crucible, washed first with 10 c.c. of 1% sulphuric acid, then with dilute alcohol, dried at 130°, and weighed as lead sulphate. Potassium salts cause the results to be as much as 50% too high, but most common metals do not interfere. To separate small quantities of lead as sulphate from large quantities of foreign metals, the following procedure is recommended. The solution containing the metals as nitrates together with 1 c.c. of normal nitric acid in 25 c.c. are treated with 25 c.c. of 95% alcohol, then with 5 c.c. of 10% ammonium

sulphate solution. After remaining over-night, the precipitate is filtered, washed, dried, and weighed as before. The method is applicable to the estimation of lead in brass and zinc. [Cf. *J.S.C.I.*, 1923, 122A.]

A. R. P.

The Iodometric Titration of Mercuric Chloride. I. M. KOLTHOFF (*Pharm. Weekblad*, 1923, **60**, 18—20).—The method proposed by Kolthoff and Keijzer (A., 1921, ii, 66), namely, reduction by alkaline hydrogen peroxide solution, acidification, solution of the separated mercury by excess of iodine and titration of the excess with thiosulphate, was found very tedious in some cases, from the long time required to dissolve the mercury. Better results are obtained by using barium hydroxide for the peroxide treatment; the mixture must be boiled and well shaken; after cooling, iodine is added to the alkaline liquid, which is acidified, after the mercury is dissolved, for titration of the excess.

S. I. L.

Sensitive Reactions of Copper and certain Phenols (Quinol and α-Naphthol). J. ALOY and A. VALDIGUIÉ (*Bull. Soc. chim.*, 1922, **31**, 1176—1179).—Dilute aqueous solutions of quinol are coloured blue by the presence of a trace of copper, slowly at the ordinary temperature and more quickly on being heated. The intensity of the coloration is proportional to the concentration of copper, and the test must be carried out in neutral or feebly acid solution. It appears to be specific for copper, as tests with other metals failed to produce the characteristic effects. The author has devised a colorimetric method for estimating copper, based on this reaction. The action is also specific for quinol among phenols, and sufficiently sensitive to detect 0·1 mg. of that substance. Copper salts are also readily detected by α-naphthol, which gives a violet coloration under conditions similar to those in the case of quinol. The colour, however, is quite distinct, and is not given by β-naphthol. The blue substance produced in the case of quinol is not extracted by ether or chloroform. The authors suggest that it may be a compound of quinol or of one of its oxidation products with the copper salt. [Cf. *J.S.C.I.*, 1923, Feb.]

H. J. E.

Precipitation and Titration Method for the Estimation of Copper in Alloys. BR. WINKLER (*Chem. Ztg.*, 1922, **44**, 1137).—The alloy is dissolved in a mixture of nitric acid and hydrochloric acid, the solution is diluted, treated with sodium potassium tartrate and an excess of sodium hydroxide, and then boiled with the addition of hydroxylamine hydrochloride. The precipitated cuprous oxide is collected, washed, dissolved in hydrochloric acid, oxidised with nitric acid, the solution is evaporated with the addition of sulphuric acid, and the copper estimated iodometrically.

W. P. S.

Estimation of Aluminium as Phosphate. G. E. F. LUNDELL and H. B. KNOWLES (*J. Ind. Eng. Chem.*, 1922, **14**, 1136—1137).—Estimations of aluminium as phosphate are generally in error.

Acceptable results are possible when only a few mg. of aluminium are involved. High values are the rule when more than 5 mg. of aluminium are precipitated by any of the usual procedures. Excessive washing of the precipitate or the use of a weak acid for washing leads to low values, as does the precipitation with only a moderate excess of the precipitant, or precipitation in alkaline solution. Under these conditions, iron behaves like aluminium, whilst titanium invariably yields low values. The precipitation of aluminium in the presence of macerated paper facilitates the washing of the precipitate. H. C. R.

Estimation of Manganese, Chromium, and Nickel in Steel. ALOIS EDER and HANS EDER (*Chem. Ztg.*, 1922, **46**, 1085—1086).—A quantity of 0·5 g. of the steel is dissolved in 25 c.c. of dilute sulphuric acid with the addition of 2 c.c. of silver nitrate solution (2·5 g. per litre); 5 c.c. of a mixture of nitric acid and phosphoric acid (equal volumes) are added, and the solution is evaporated to expel nitric acid. After cooling, the solution is diluted, treated with 3 g. of ammonium persulphate, boiled for five minutes, again cooled, 5 c.c. of sodium chloride solution (25 g. per litre) are added, and the permanganate is titrated with standardised arsenious acid solution. The titrated solution is then boiled for twenty-five minutes to decompose the excess of persulphate, cooled, a known volume of standardised ferrous ammonium sulphate solution is added to reduce the chromate, and the excess is titrated with permanganate solution. The mixture is then treated with 50 c.c. of sodium pyrophosphate solution (150 g. per litre); the precipitate formed is dissolved by the addition of ammonia, excess of the latter is neutralised with sulphuric acid, a few drops of ammonia are added to dissolve any precipitate formed, and, after the addition of 5 c.c. of potassium iodide solution (40 g. per litre), the turbid solution is titrated with standardised potassium cyanide solution, the end-point being denoted by the solution becoming clear. This titration, after allowance for the silver added originally, gives the quantity of nickel present. W. P. S.

A Micro-method for the Estimation of Iron in Colloidal Solutions. I. NEWTON KUGELMASS (*Bull. Soc. Chim. Biol.*, 1922, **4**, 577—583).—To a known volume of the solution, concentrated hydrochloric acid and an oxidising agent (perhydrol) are added. The mixture is boiled and *iso*amyl alcohol added, followed by ammonium thiocyanate, when the ferric thiocyanate passes completely into the amyl alcohol layer. This is pipetted off and compared in a colorimeter with a similar amyl alcohol solution prepared from a known aqueous solution of ferric-ions. W. O. K.

The Electrometric Estimation of Cobalt with Silver Nitrate. ERICH MÜLLER and HANS LAUTERBACH (*Z. anal. Chem.*, 1923, **62**, 23—28).—Cobalt may be estimated in a similar manner to nickel (A., 1922, ii, 875) by addition of an excess of standard potassium cyanide solution to a neutral solution of the cobalt salt, followed by titration of the excess by silver nitrate, the end-

point being ascertained conductometrically. The cobalt compound formed in the first stage of the process is $K_3Co(CN)_5$, whereas nickel forms $K_2Ni_1(CN)_4$; a larger amount of cyanide must therefore be added than is required in the nickel estimation. The presence of free ammonia in the cobalt solution leads to slightly low results. A. R. P.

Estimation and Separation of Titanium, Columbium, Tantalum, and Zirconium. WILLIAM P. HEADDEN (*Proc. Colorado Sci. Soc.*, 1917, **11**, 185—201).—The gravimetric estimation of titanium in the presence of columbic acid appears to be most difficult, if not impossible, but small quantities of titanium may be estimated colorimetrically by means of hydrogen peroxide. To separate titanic acid from tantalic acid, the two substances are fused with potassium hydrogen sulphate, the mass is dissolved in water and hydrofluoric acid, the solution neutralised with ammonia, ammonium fluoride, ammonium hydrogen carbonate, and hydrogen peroxide are added, and the boiling mixture is poured into hot ammonium carbonate solution. The tantalic acid is precipitated whilst the titanic acid remains in solution; to ensure complete separation the precipitate should be dissolved and re-precipitated. A method for the approximate separation of tantalic acid from columbic acid depends on the fact that tantalic acid is precipitated when its hydrofluoric acid solution is treated at 70° with an excess of ammonium hydrogen carbonate; under these conditions, columbic acid remains in solution. Titanic acid may be separated from zirconia by dissolving the freshly precipitated oxides in ammonium fluoride solution and then adding an excess of ammonia; the titanic acid is precipitated completely and the zirconia remains in solution. When a solution containing zirconia and columbic acid is treated with ammonium fluoride and ammonium hydrogen carbonate, and boiled, the columbic acid is precipitated; this method may also be used for the separation of zirconia from tantalic acid. W. P. S.

Estimation of Bismuth. KÖSTER (*Chem. Ztg.*, 1923, **47**, 22).—Small quantities of bismuth in lead may be detected by cupelling 25 g. of the mètal and moistening the dark spot in the middle of the cupel with dilute hydriodic acid. If bismuth is present, this spot becomes surrounded by a red ring, the extent and intensity of which depend on the quantity of bismuth present. To carry out a quantitative estimation, quantities of 25 g. of pure lead are cupelled with varying amounts of bismuth and the colour produced in the assay is compared with this series of standards. The hydriodic acid is conveniently prepared by passing hydrogen sulphide into water in which iodine is suspended and filtering off the precipitated sulphur. The method is applicable to the detection and estimation of bismuth in ores which are fused with litharge, carbon, and fluxes exactly as in the ordinary gold and silver assay, and the lead button is cupelled as described above. A. R. P.

Rapid Estimation of Bismuth in Urine. DOMENICO GANASSINI (*Boll. Chim. Farm.*, 1922, **61**, 705—708).—The author replies

to Dezani's criticisms (*Biochim. Terap. sperim.*, 1922, **9**, 267) on his method for the estimation of bismuth in urine (A., 1922, ii, 590). Dezani's method, based on the yellow coloration obtained on addition of potassium iodide to a very dilute solution of a bismuth salt in presence of hydrochloric acid, gives uncertain results when applied to urine. T. H. P.

Use of Textile Fibres in Qualitative Chemical Analysis. V. Detection of Gold by means of Stannous Chloride-Pyrogallol Viscose Fibres. HOWARD IRVING COLE (*Philippine J. Sci.*, 1922, **21**, 361—364; cf. A., 1918, ii, 129).—Viscose fibres treated with stannous chloride and pyrogallol may be used for the detection of very small quantities of gold; a red or blue coloration is obtained when the fibre is immersed in a drop of solution containing as little as 0·00002 mg. of gold and the solution allowed to evaporate to dryness. More concentrated solutions yield a red or purple coloration at once. W. P. S.

Direct Estimation of the Caoutchouc Hydrocarbon as the Bromide. M. PONTIO (*Chim. et Ind.*, 1922, **8**, 1211—1212).—A solution of 0·2 g. of the raw caoutchouc in 20 c.c. of xylene is treated with 50 c.c. of a solution of bromine in carbon tetrachloride or chloroform (3 vols. to 247 vols.). After one-quarter of an hour, 250 c.c. of acetone are added, the mixture being agitated and filtered immediately, using "tared" filter-papers. The precipitate is washed repeatedly with acetone and finally with alcohol before being dried at 70—80°. After subtracting the weight of residue obtained on incineration, the weight of the product is multiplied by 0·317 for conversion into caoutchouc, the composition of the product approximating to $(C_{10}H_{16})_3Br_{11}$. For this estimation, it is preferable to remove the natural resins previously by extraction of the solid caoutchouc, and also the protein matter by sedimentation or filtration of the solution. D. F. T.

Use of Iodine in the Estimation of Dextrose, Lævulose, Sucrose, and Maltose. F. A. CAJORI (*J. Biol. Chem.*, 1922, **54**, 617—627).—Dextrose may be estimated iodometrically by Bougault's method (A., 1917, ii, 395) in the presence of both lævulose and sucrose. At the ordinary temperature, the oxidation is complete in twenty-five minutes. To avoid risk of enolisation, the concentration of sodium carbonate should not exceed 1—1·5%. When used in conjunction with estimations based on the copper-reducing power, this method may evidently be applied to the estimation of mixtures of the above three sugars. For this purpose, hydrolysis of the sucrose should be effected by heating for two hours at 60° with 1% hydrochloric acid; at higher temperatures, some decomposition of lævulose occurs. In the iodometric estimation of maltose, thirty-five minutes are required for the oxidation. The estimation may also be made indirectly after hydrolysis to dextrose by freshly prepared yeast maltase, provided corrections are made for the reducing power of the maltase preparation. Since maltose is not appreciably hydrolysed under the conditions used

above for sucrose, the method may possibly be extended to include mixtures of all four sugars (cf. also Judd, A., 1920, ii, 395; Baker and Hulton, A., 1921, ii, 417). E. S.

Methods for the Estimation of Starch in Small Quantities in Plant Tissues [Cantaloupe seeds]. F. E. DENNY (*J. Assoc. Off. Agric. Chem.*, 1922, **6**, 175—191).—The most suitable method for the estimation of starch in quantities of 0·1—1·0% is as follows. The ground cantaloupe seeds are extracted with cold light petroleum and oven dried. Starch is extracted with saturated calcium chloride solution at the boiling temperature. Aliquot portions of the extract are treated with $N/10$-iodine drop by drop until a permanent blue colour appears (satisfying the non-starch iodine-absorbing substances) and then with excess of standard $N/50$-iodine. After remaining over-night, the precipitate is separated by centrifuging and washed with potassium iodide solution. Absorbed iodine is estimated by boiling the precipitate with excess of thiosulphate solution ($N/200$) and titrating with standard iodine. Comparison is made with figures obtained with pure starch. The average ratio, iodine absorbed : starch, was 0·11, tending to decrease in smaller concentrations. The method of Scales (A., 1919, ii, 435) would appear capable of refinement, to give considerably increased sensitivity. A. G. P.

Formic Acid. I. Gravimetric Estimation of Formic Acid. FR. AUERBACH and H. ZEGLIN (*Z. physikal. Chem.*, 1922, **103**, 161—177).—The gravimetric estimation of formic acid by means of mercuric chloride has been investigated and the original method improved in several particulars. The modified method for this estimation is carried out as follows. The solution of formic acid or formate (50—100 c.c.) is neutralised in an Erlenmeyer flask with either sodium carbonate or hydrochloric acid if it is acid or alkaline in reaction. Then 1 c.c. of N-hydrochloric acid is added followed by 3 g. of crystalline sodium acetate. If the amount of formic acid present is greater than 0·1 g., the amount of sodium acetate must be correspondingly increased, whilst if it is less than 0·005 g. the acetate must be reduced to 1 g. Mercuric chloride is then added in 5% solution in quantity equal to twelve times the amount of formic acid present and an additional excess of 12 mg. for each c.c. of total solution in the flask. If the solution contains salicylic acid or similar acid, then 1 mg. of sodium chloride is added for each c.c. of the total solution in the flask. The flask is covered with a watch glass and heated for two hours on a rapidly boiling water-bath. The precipitated mercurous chloride is filtered in a platinum filter crucible, washed with water at 40—50°, and finally with alcohol. The crucible is dried for forty-five to sixty minutes at 95—100° and weighed. The weight of the precipitate multiplied by the factor 0·09745 gives the weight of formic acid. This method yields excellent results for quantities of formic acid down to 1 mg. Should the formic acid to be estimated be present in ethereal solution it is extracted with an aqueous solution of

sodium acetate and the estimation carried out as above in the aqueous solution. J. F. S.

[Estimation of Formic Acid]. FR. AUERBACH and H. ZEGLIN (*Z. physikal. Chem.*, 1922, **103**, 200—237).—See this vol., ii, 61.

Estimation of Formic Acid in the Urine. ETHEL M. BENEDICT and G. A. HARROP (*J. Biol. Chem.*, 1922, **54**, 443—450).—The method of Dakin, Janney, and Wakeman (A., 1913, i, 679) has been modified to avoid the preliminary extraction with ether. The urine (100 c.c.) is diluted with water (500 to 600 c.c.), treated with a 20% copper sulphate solution (100 c.c.), made just alkaline by the addition of a 10% suspension of calcium hydroxide, and diluted to 1 litre. After fifteen to thirty minutes, the mixture is filtered and an aliquot part of the filtrate (600 c.c.) made distinctly acid with 85% phosphoric acid and then steam distilled, the distillate (2 litres) being collected in $0{\cdot}1N$-sodium hydroxide (15 to 20 c.c.). The distillate is evaporated to dryness, dissolved in water (100 c.c.), and an aliquot part (90 c.c.) made just acid by the addition of $0{\cdot}1N$-HCl and treated with 10 c.c. of a mercuric chloride mixture (1 litre contains 200 g. mercuric chloride, 80 g. sodium chloride, and 300 g. sodium acetate). It is then heated for one hour on a water-bath under reflux. The precipitated mercurous chloride, which represents 99% of the theoretical amount, is filtered and weighed. E. S.

Differentiation of Acetic Anhydride from Glacial Acetic Acid. VICTOR E. LEVINE (*Science*, 1920, **52**, 207).—(1) The addition of a few drops of a 0·5% solution of selenium dioxide in concentrated sulphuric acid to acetic anhydride results in the formation of a brick-red, colloidal solution or precipitate of selenium. Glacial acetic acid does not react. (2) Ten drops of acetic anhydride are shaken with 2 c.c. of chloroform in which a small quantity of cholesterol has been dissolved. On the addition of 20 drops of concentrated sulphuric acid, a fleeting purple colour is developed, changing to blue and finally to deep green. With or without glacial acetic acid, a lemon-yellow colour is formed which rapidly becomes deep orange, cherry-red, or burgundy-red. A. A. E.

Estimation of Abietic Acids and of Colophony. FERDINAND SCHULZ and STANISLAV LANDA (*Bull. Soc. chim.*, 1922, [iv], **31** 1353—1360).—The method is based on the reducing action of abietic acid on mercuric acetate. A solution of about 0·5 g. of the substance in 10 c.c. of a saturated solution of mercurous acetate in glacial acetic acid is warmed for an hour at 50° with the freshly prepared mercuric acetate reagent prepared by dissolving 3 g. of mercuric oxide in 50 c.c. of glacial acetic acid likewise saturated with mercurous acetate. After keeping for a further hour, the precipitate of mercurous acetate is collected, washed, and dissolved in 20% nitric acid, and the mercury in the solution thus obtained is estimated by Votoček's method—oxidation by permanganate addition of sodium chloride solution, and titration of the excess by mercuric nitrate solution in presence of sodium nitroprusside

The mean value found for the equivalent of 1 g. of colophony was 1·84 g. of mercuric oxide. Colophony in admixture with shellac, and palm oil or other soap-making materials, can be estimated by this method to an accuracy of about $\pm 10\%$. The estimation of crystallised abietic acid from American colophony gave an equivalent of 1·974 g. of mercuric oxide per g. of acid, corresponding approximately with the ratio $3HgO : C_{20}H_{30}O_2$. The oleosylvic acid, m. p. 167—169°, $[\alpha]_D$ +56·2°, from the resin oil was apparently a mixture of reducing and inert acids, as 1 g. reduced only about 0·36 g. of mercuric oxide. G. F. M.

Detection of Acetoacetic Acid in Diabetic Urine. G. Favrel (*Ann. Chim. Analyt.*, 1922, **4**, 337—338).—The urine is acidified with hydrochloric acid and extracted with ether; the ethereal solution is evaporated, the residue dissolved in water, treated with calcium carbonate, and the mixture filtered. If acetoacetic acid (enolic form) is present, the filtrate yields a red coloration with ferric chloride. W. P. S.

Microchemical Detection of Fumaric Acid. L. van Itallie (*Pharm. Weekblad*, 1922, **58**, 1312—1314).—Fumaric acid may be detected by the characteristic appearance of its thallium, lead, and copper salts under the microscope. The first is least satisfactory, requiring definite concentrations of the reagents. The lead salt forms thick, colourless prisms, the copper salt light blue aggregates of needles. S. I. L.

Estimation of Tartaric Acid. André Kling (*Ann. Chim.*, 1922, [ix], **18**, 189—216).—Only *d*-tartaric acid occurs naturally and it cannot be precipitated quantitatively as calcium or lead tartrate. But after addition of an equivalent amount of the *l*-acid, quantitative precipitation is practicable in presence of dilute acetic acid. The method of estimation is based on addition to the natural acid of an excess of the *l*-acid or of one of its salts, followed by calcium acetate solution. By this means all the *d*-acid is precipitated as calcium racemate, carrying with it some calcium *l*-tartrate. The precipitate is dissolved in dilute hydrochloric acid and, on addition of sodium acetate, pure calcium racemate is obtained. The precipitate is dissolved in boiling 10% sulphuric acid and titrated with standard permanganate, half the quantity of acid found corresponding with that of the *d*-acid originally present. H. J. E.

Detection of Ethyl Phthalate and Phthaleins. Ralph L. Calvert (*Amer. J. Pharm.*, 1922, **94**, 702—703).—Ethyl phthalate being used as a denaturant for alcohol for use in perfumery in America, its detection is a matter of interest. A satisfactory test is performed as follows: To 3—5 c.c. of the sample 5—10 drops of phenol and 10 drops of sulphuric acid are added, and the mixture is gently heated until most of the alcohol has distilled off, and a red liquid remains. After cooling, 15—25 c.c. of water are added, when, if ethyl phthalate is present, the red colour disappears and a turbid liquid is obtained which becomes red on addition of sodium

hydroxide (phenolphthalein reaction). The reaction is quite delicate, as 1 c.c. of a 0·1% solution gives a distinct coloration.

G. F. M.

The Estimation of Milk in Milk Chocolate. J. Grossfeld (*Z. Unters. Nahr. Genussm.*, 1922, **44**, 240—244).—The quantity of butter fat in milk chocolate can be arrived at from the Reichert-Meissl value of the total fat extracted with ether. The quantity of milk-protein present can be calculated from the percentage of ash (a) and the percentage of calcium oxide (b) in the chocolate according to the formula $26{\cdot}1b-1{\cdot}16a$, or alternatively, if N is the percentage of total nitrogen in the chocolate, from the formula $21{\cdot}4b-1{\cdot}35N$. Details of the method used for estimating the calcium oxide are given. Comparison of the milk-protein as estimated by the two methods outlined above and of casein as estimated by Baier and Neumann's method (*ibid.*, 1909, **18**, 13) show in general satisfactory agreement.

H. C. R.

Analytical Applications of the Reaction between Sulphites and Aldehydes. José Estalella (*Anal. Fís. Quím.*, 1922, **20**, 271—282).—The compounds of aldehydes with sodium hydrogen sulphite are slowly hydrolysed on keeping with liberation of sodium hydroxide. A 1% solution of sodium sulphite in the presence of phenolphthalein is proposed as a reagent for aldehydes. Similarly, formaldehyde in the presence of phenolphthalein may be used as a reagent for sulphites. The positive reaction consists in the development of a pink colour. The reaction is unsuitable as a basis for the quantitative estimation of sulphites. Small quantities of aldehydes may be estimated by means of it, using a colorimetric method.

G. W. R.

Methods of Estimation of Formaldehyde by Oxidation. Raoul Gros (*J. Pharm. Chim.*, 1922, [vii], **26**, 415—425).—The method of the French Codex is very inaccurate owing to incomplete oxidation of the aldehyde on the one hand, and to the further oxidation of some of the formic acid to carbonic acid on the other. Romijn's method, oxidation with iodine in presence of alkali, is fairly accurate if the prescribed conditions are closely adhered to, but the presence of acetone would interfere. A method uninfluenced by the presence of either acetone or formic acid consists in adding to 5 c.c. of approximately 1% formaldehyde solution, 35 c.c. of potassium mercuric iodide solution (2·71% $HgCl_2$, and 7·2% KI), and 20 c.c. of 27% sodium hydroxide solution. The red precipitate gradually changes to a greyish precipitate of mercury, and after ten minutes the liquid is carefully acidified with hydrochloric acid, a known excess of $N/10$-iodine is added to oxidise and dissolve the mercury, and the excess is titrated back with $N/10$-thiosulphate. The accuracy of this and other methods for the estimation of formaldehyde can conveniently be controlled by an analysis of formaldehyde sodium bisulphite, $CH_2O,NaHSO_3,H_2O$, the sulphite being estimated by titration with iodine in presence of potassium hydrogen carbonate, under which conditions the

aldehyde is practically unattacked, and is then estimated by the method under investigation, and the result, of course, should be in accord with that obtained by the sulphite estimation.

G. F. M.

Comparative Tests on the Methods in Use for the Estimation of Formaldehyde in Formalin. F. Mach and R. Herrmann (*Z. anal. Chem.*, 1923, **62**, 104—137).—The literature of the iodine, hydrogen peroxide, sodium sulphite, and ammonium salt methods of determining formaldehyde and its polymerisation products in commercial formalin is reviewed in detail and a large number of comparative results obtained by each of the methods on different samples are tabulated. The results obtained by the first three methods are in good agreement, whereas those obtained by the fourth method are about 0·5—1·0% lower than these. The presence of ethyl alcohol, acetaldehyde, and acetone leads to very erroneous results in the iodine method, whereas the influence of small quantities of these substances is comparatively slight in the sulphite method and almost negligible in the peroxide method. Larger amounts of acetone or acetaldehyde than 4%, however, give low results when the assay is allowed to remain the normal time and high results if left for some hours before titration. In all the methods the choice of indicator is important, azolitmic acid in the peroxide method and rosolic acid in the sulphite and ammonium salt methods being the most suitable. [Cf. *J.S.C.I.*, 1923, 118A.]

A. R. P.

Detection of Santonin. F. Utz (*Süddeutsch. Apoth.-Ztg.*, 1922, **62**, 77—78).—Santonin is sprinkled into a hot solution prepared by adding one or two drops of dilute ferric chloride solution to 1 c.c. of distilled water and mixing with 1 c.c. of concentrated sulphuric acid, and the liquid shaken with amyl alcohol, which assumes a blood-red colour. The methods described by Thaeter (A., 1898, ii, 59), Jaworowski (*Chem. Ztg.*, 1897, 269), Smith (*Chem. Zentr.*, 1871, 486), Banfi (*Annalen*, **91**, 112), Schermer (*Pharm. Z. Russ.*, 1893, **32**, 120), Mindes (*Pharm. Post*, **44**, 687), and Neuhaus (*Deut. med. Woch.*, 1906, 466), and that of the German pharmacopœia are criticised.

Chemical Abstracts.

Compound of Antipyrine and Xanthydrol. René Fabre (*J. Pharm. Chim.*, 1922, [vii], **26**, 372—376).—By the interaction at ordinary temperatures of equimolecular proportions of xanthydrol in solution in methyl alcohol and antipyrine in solution in acetic acid, a *xanthylantipyrine* is formed and is slowly precipitated in fine needles, m. p. 178—179°. The formation of this derivative may be utilised to detect antipyrine in presence of pyramidone, quinine, etc., but, owing to its slight solubility, the method cannot be used for its estimation. The presence of antipyrine in urine would cause an error in the estimation of urea by means of xanthydrol unless it is previously removed by defecating the urine with an acetic acid solution of potassium mercuric iodide.

G. F. M.

Modification of Folin, Cannon, and Denis's Colorimetric Method for the Estimation of Adrenaline. SAKUJI KODAMA (*J. Biochem.* [*Japan*], 1922, **1**, 280—287).—One c.c. of the uric acid reagent and 10 c.c. of a 20% solution of sodium carbonate are added to the solution under examination, and diluted to 50 c.c. with water. After two minutes the colour is compared in a Duboscq colorimeter with a standard solution containing 4 c.c. of 0·01% solution of water-blue, 4 c.c. of a 0·01% solution of nigrosine, 10 c.c. of a 10% solution of crystalline copper sulphate, 10 c.c. of hydrochloric acid (*d* 1·050), and water to 100 c.c. This solution, which must be standardised against uric acid, when set at 20·6 mm. should match the colour developed by 0·3 mg. of uric acid or 0·1 mg. of adrenaline. CHEMICAL ABSTRACTS.

Sensitiveness of some Cyanide Reactions. JOHN B. EKELEY and ICIE C. MACY (*Proc. Colorado Sci. Soc.*, 1919, **11**, 269—275).—The Prussian blue test will detect the presence of 1 part of hydrocyanic acid in 170,000 parts of solution; if the test is applied to the distillate obtained after acidifying the solution with tartaric acid, 1 part in 1,700,000 parts may be detected. The sensitiveness of the hanging drop test with silver nitrate is 1 part of hydrocyanic acid in 19,000,000 parts, whilst the Schönbein (guaiacum paper) test will detect 1 part in 55,000,000 parts. Chlorine, bromine, hydrogen peroxide, and hydrochloric acid do not yield a reaction with the Schönbein test when the dilution is greater than 1 part per million. W. P. S.

Detection of Urobilin in Blood and in the Cerebrospinal Fluid. GEORGES RODILLON (*Bull. Soc. Chim. Biol.*, 1922, **4**, 474—475).—To 1 vol. of serum from the blood under examination, or of the cerebrospinal fluid, 1 vol. is added of a reagent consisting of a saturated solution of zinc acetate in 95% alcohol strongly acidified with acetic acid. To the filtered liquid thus freed from protein, 1 drop for every 5 c.c. of solution of a 1 in 150 alcoholic iodine solution is added, followed by one-tenth of a volume of chloroform. After agitation, the alcoholic chloroform layer which separates will contain a zinc compound of urobilin if the latter is present, and it is detected by directing a pencil of light concentrated by a converging lens on to the chloroform solution placed in front of a dark background. In presence of the minutest traces of urobilin a green fluorescence will be observed, and a spectroscopic examination will show very clearly a dark band in the blue-green between the *E* and *F* lines, and close to the latter. In presence of larger quantities of urobilin the chloroform layer will show a rose-coloured tint. The test can be carried out with very small quantities of serum, etc., as little as 0·5 c.c. being sufficient.

G. F. M.

General and Physical Chemistry.

Spectrochemical Investigations on Polynuclear Aromatic Compounds in Solution. F. KROLLPFEIFFER (*Annalen*, 1923, **430**, 161—229).—Largely a statement in tabular form of the numerical results of the author's measurements of the refractive indices in various solvents of a large number of derivatives of benzene, naphthalene, anthracene, and other polynuclear systems (cf. following abstract). C. K. I.

Spectrochemical Peculiarities and Constitution of Naphthalene, Anthracene, Phenanthrene, and Fluorene. K. VON AUWERS and F. KROLLPFEIFFER (*Annalen*, 1923, **430**, 230—268).—In this paper the spectrochemical measurements referred to in the preceding abstract, along with similar numerical data obtained at earlier dates and some new measurements, are collected together and discussed from the point of view of their bearing on the constitution of the various basic ring systems. The authors favour structures for naphthalene and anthracene in which only one ring has full aromatic character, and the usually accepted structures for phenanthrene and fluorene. As regards the effect of substitution in naphthalene on spectrochemical properties, the conclusions are drawn (1) that large increases in the specific refraction run parallel with large dispersion; (2) that the introduction of alkyl, alkoxyl, carbalkoxyl groups, and halogens has but little effect either on the exaltation of the refraction or dispersion; (3) that the effect of halogens is greater than in derivatives of benzene, and (4) β-derivatives have as a rule a stronger exaltation in specific refraction than the corresponding α-derivatives.

C. K. I.

"Aromatic" Carbon. K. VON AUWERS (*Ber.*, 1923, **56**, [*B*], 69—76; cf. von Steiger, A., 1921, ii, 473; 1922, ii, 616; von Auwers, A., 1922, ii, 98).—A further criticism of von Steiger's hypothesis that an essential difference exists between aliphatic and aromatic carbon atoms.

The regularities observed in the thermochemistry of aromatic hydrocarbons do not necessitate the supposition of the tervalency of carbon, but are equally reconcilable with the quadrivalency of the element (cf. Wibaut, A., 1922, ii, 239). They do not necessitate the hypothesis that the C–C and C–H linkings in aromatic hydrocarbons are equivalent from the point of view of energy which, moreover, is not in harmony with the principle of the distribution of energy of combination adopted by von Steiger (*loc. cit.*). It is only proved that the mean energy of formation of the individual linkings can be regarded as equal for purposes of calculation; this is in harmony with the similarity in the constitution of the molecules, but does not necessitate any particular assumption with regard to the nature of carbon in these compounds.

From the spectrochemical point of view, it is shown in detail that the molecular refractions of anthracene and phenanthrene differ from one another to a degree which is completely outside the limits of experimental error, whereas they should be identical if von Steiger's hypothesis is correct. In general, von Steiger regards discrepancies between the observed values and those calculated with the aid of the "normal" equivalents as defects, whereas the whole history of spectrochemistry shows that such discrepancies are of the maximum value in throwing light on the constitution of the compounds under examination. Von Steiger's method of calculating the molecular refractions is quite unsuitable for the homologues of benzene, since the difference increases with increasing number of side chains.

Von Steiger's conception of the peculiar nature of "aromatic" carbon rests on the work of Debye and Scherrer, on the crystalline structure of graphite, the additivity of the heats of combustion of certain purely aromatic hydrocarbons, and the supposed additivity of their molecular refractions. Arguments based on the two latter points have been shown to be invalid, whilst Debye and Scherrer's observations do not depend on the existence of two differing types of carbon atom, but on the formation of different types of molecule owing to the differing mode of union of identical carbon atoms. Further, exception is taken to the sharp differentiation of aliphatic and aromatic carbon, since this is not justifiable on purely chemical grounds and can only be applied to two extreme types of compounds which are not chemically distinctly separated.

H. W.

The Molecular Refraction of Anthracene. F. KROLL-PFEIFFER (*Ber.*, 1922, **55**, [*B*], 77—83).—The molecular refraction of anthracene dissolved in quinoline has been determined, the calculations being made in accordance with the formula $Mr_L=M[r_{LS}\times 100/p-r_{LM}(100-p)/p]$, in which M is the molecular weight of the dissolved substance, r_L its specific refraction according to Lorenz and Lorentz, r_{LS} the specific refraction of the solution, r_{LM} that of the solvent, and p the percentage of solute. The mean value $M_D^{99\cdot5}=65\cdot3$; this is considerably higher than that observed by von Steiger (A., 1922, ii, 616) for anthracene dissolved in naphthalene, which is in agreement with the previous observations of Chilesotti. The discrepancy does not appear to be attributable to the particular solvent used, since the molecular refractions of the closely allied 1-methyl- and 9-ethyl-anthracenes are almost identical when the determinations are made with the molten materials or with their solutions in quinoline or naphthalene. Re-determination of the molecular refraction of anthracene dissolved in naphthalene has given values which agree excellently with those observed when quinoline is used as solvent, and are much higher than those found by von Steiger and Chilesotti; the error in the observations of the former appears to lie in the observation of the refractive indices, the latter in that of the density.

The values obtained for the molecular refraction of phenanthrene dissolved in benzene or naphthalene agree with those observed by von Steiger and Chilesotti. H. W.

Calculation of the Hydrogen Dissimilar Spectra from the Inner Movements of the Electrons. II. E. Fues (*Z. Physik*, 1923, **12**, 1—12).—A continuation of a theoretical discussion (this vol., ii, 1), in which it is shown that it is possible to calculate the terms of the Röntgen and optical spectra from the movements of the electrons in a central field of force, and to derive the potential curve of the atomic field. The sodium spectrum is considered in detail, and the terms in its spectrum are deduced from the potential curve. The agreement for the quantum numbers of the 3_1, 4_1, 5_1, 6_1, 3_2, 4_2, 5_2, 6_2, 3_3, 4_3, 5_3, 6_3, and 4_4 members, which is within 3%, is a demonstration of the correctness of the recent views on the origination of series spectra. W. E. G.

Visible and Ultra-red Radiation of Hydrogen. Frederick Sumner Brackett (*Astrophys. J.*, 1922, **56**, 154—161).—The radiation from the central section of a long discharge tube has been analysed by means of a rock-salt prism spectrometer, and a sensitive vacuum thermo-junction. Three (probably four) additional members of the Paschen series have been observed, as well as the first two members of a new series corresponding with $\nu=N(1/4^2-1/m^2)$, where $m=5$, 6. These two lines, at λ $4{\cdot}05\pm0{\cdot}03\mu$ and $2{\cdot}63\pm0{\cdot}02\mu$ are due, according to Bohr's theory, to an electron falling into the fourth from the fifth and sixth rings of the hydrogen atom. Certain unidentified lines are recorded, and it was observed that, with increase of current, the first Paschen line increased in intensity more rapidly than H_α. A. A. E.

New Bands in the Spectrum of Silicon. Angel del Campo and José Estalella (*Anal. Fis. Quim.*, 1922, **20**, 586—588; cf. del Campo, *ibid.*, 1915, **13**, 98).—Seven new bands are described in the spectrum of silicon. They occur between λ 2255·85 Å. and λ 2146·0 Å., and appear to be composed of lines of variable intensity. A complete list of the components of the silicon spectrum is given. G. W. R.

The Spectrum of Neutral Helium. W. M. Hicks (*Nature*, 1923, **111**, 146).—A criticism of the formula employed by Silberstein (this vol., ii, 46) to express the diffuse series HeD′. A. A. E.

The Visibility of Individual Spectra. F. H. Newman (*Phil. Mag.*, 1923, [vi], **45**, 293—299; cf. this vol., ii, 46).—The relative visibility of the spectra of the vapour from alkali amalgams at 200° is affected by the nature of the electrical discharge through the vacuum tube. The spectrum of the alkali metal is always well developed with the ordinary uncondensed discharge, but is completely masked by the mercury spectrum when the condensed discharge is used. With the latter, the resultant increase in electrical energy is sufficient to impart higher velocities to the colliding electrons

during their mean free path, and to ionise the mercury atoms, although these have higher ionisation potentials than the atoms of the alkali metals. The energy attained is sufficient to remove two or more electrons, as is shown by the production of enhanced lines. W. E. G.

Revision of the Series in the Spectrum of Strontium. F. A. SAUNDERS (*Astrophys. J.*, 1922, **56**, 73—83).—Measurements have been made of the spectrograms of light from a great variety of sources, and revised wave-lengths are given for most of the 180 lines from 0·22 to 3·06 μ, including about 70 new lines. Accurate determinations have been made of the limits of all the series, and the various terms have been calculated. About half of the twenty series mentioned are believed to be new, and there is evidence of the existence of new types of singlet series corresponding with the formulæ $(1P)-(mX)$, $(1p)-(mX)$, $(1P)-(mY)$, etc. The terms are all large, so that the series cannot be of the kind suggested by Sommerfeld. In the case of calcium, three singlet lines are found to correspond accurately with $(1P)-(mX)$, $(1p_1)-(mX)$, and $(1p_2)-(mX)$, where (mX) is 8584·8, thus indicating a series similar to that of strontium. A. A. E.

Structure of the Spectrum of Scandium. MIGUEL A. CATALÁN (*Anal. Fís. Quím.*, 1922, **20**, 606—623).—The lines in the spectrum of scandium fall into two classes, namely, those forming doublets and those forming triplets. Sommerfeld's displacement rule holds for scandium, since its enhanced spectrum is analogous to the arc spectrum of calcium. The multiplets (cf. A., 1922, ii, 726) are divided into "multidoublets" and "multitriplets." Complete lists are given of the lines in the spectra of the neutral and ionised atom, respectively. G. W. R.

The Structure of the Arc Spectra of the Elements of Columns VI and VII in the Periodic Table. M. A. CATALÁN (*Compt. rend.*, 1923, **176**, 84—85).—It has previously been shown (A., 1922, ii, 726) that the manganese spectrum shows three diffuse triplets, consisting of nine rays instead of six, due to the fact that the diffuse term d is quintuple instead of triple. It is now shown that this is not a property peculiar to manganese, but is common to other elements. The arc spectrum of chromium is very complex and presents several systems of series. Two of these, determined for the first time, are tabulated. They are almost identical, the one being displaced with respect to the other by a constant quantity, C=4436·4. The diffuse terms are quintuple and give nine rays as for manganese. W. G.

The Structure of the Spectrum of Chromium. A. DE GRAMONT (*Compt. rend.*, 1923, **176**, 216—217).—The author directs attention to the fact that he predicted that in the spectrum of chromium there would be two triplets, one corresponding with the neutral atom and the other with the ionised atom, and that this prediction has now found confirmation by the measurements made by Catalán (preceding abstract). W. G.

The Structure of the Arc Spectra of Molybdenum, Selenium, and Chlorine. M. A. Catalán (*Compt. rend.*, 1923, **176**, 247—248).—The arc spectrum of molybdenum is extremely complex. The diffuse term is quintuple and the number of rays is nine. The rays of the triplet of the principal series are the ultimate rays of Gramont. The diffuse triplets of selenium are regarded as exceptional by the number, the intensity, and the position of their satellites. The spark spectrum of chlorine shows triplets. The photograph of the spectrum shows the presence of at least three components in the first ray, although the tables give a number of components equal to 1+3+2. Thus the diffuse term of the elements of columns VII and VI of the periodic table is quintuple and the number of rays which form the diffuse triplets is nine.
W. G.

Coincidence Method for the Wave-length Measurement of Absorption Bands. H. Hartridge (*Proc. Roy. Soc.*, 1923, [*A*], **102**, 575—587).—A spectroscope suitable for the measurement of wave-lengths of absorption bands is described. It is designed so that two similar spectra are produced, lying side by side and reversed in direction to one another. For the measurement of the mean wave-length of a band, the long wave-length edge of the band in one spectrum is brought into coincidence with the corresponding short wave-length edge in the other. The mode of calibration of the instrument to read directly in wave-lengths is described and the application of the instrument to the quantitative estimation of pigments by wave-length measurements of their absorption bands detailed. The method depends on the principle that if two pigments are present together in solution, and their respective absorption bands have different mean wave-lengths, then the mean wave-lengths of the resultant absorption bands will vary with the relative concentrations of the pigments, provided the band of one pigment is approximately similar to a band of the other, and if at no concentration do the bands appear separate. An illustration of the application of the method is given in the case of the estimation of the percentage saturation of blood with carbon monoxide. The accuracy of measurement attainable was found to be about 0·6 Å. Various sources of error are discussed.
J. S. G. T.

Absorption of Light by Chlorine. H. von Halban and K. Siedentopf (*Z. Elektrochem.*, 1922, **28**, 496—499).—A preliminary account is given of measurements of the absorption spectrum of chlorine for a large number of wave-lengths between 254 $\mu\mu$ and 643 $\mu\mu$, making use of the very sensitive method of measurement recently described by the authors (A., 1922, ii, 332). The results show that nowhere is chlorine entirely transparent, but that in all regions absorption occurs, which is generally very difficult to measure. The measurements are reproducible, although the absorption in some cases does not amount to more than 0·2—0·3%.
J. F. S.

The Quantitative Absorption of Light by Simple Inorganic Substances. II. The Chlorides of Arsenic, Antimony, and Bismuth. ALEXANDER KILLEN MACBETH and NORAH IRENE MAXWELL (T., 1923, **123**, 370—375).

The Absorption Spectra of Thallium and Indium Vapours. WALTER GROTRIAN (*Z. Physik*, 1923, **12**, 218—231).—According to the Bohr atomic theory, emission lines can occur only as absorption lines at any temperature when the initial stage in the absorption corresponds with a molecular or atomic state which is of frequent occurrence in the molecules of the gas. Absorption spectra are thus useful in throwing light on the variation in the quantum condition of gas molecules with temperature. Series schemes of the emission spectra, given for aluminium, gallium, indium, and thallium, show that for these metals, not the *s*, but the *p*-terms are the greatest of all the known terms. For thallium, at a temperature of 400°, two absorption lines of the $2p_2$ subordinate series, $\lambda=3775{\cdot}72$ and $\lambda=2767{\cdot}87$, first make their appearance, and at 500—600° other lines in this series appear. With increasing temperature, these lines broaden, probably owing to molecular (Tl_2) adsorption. At 800°, the $2p_1$ subordinate series is first observed, the order of appearance being $\lambda=5350{\cdot}46$, and then the doublet $\lambda=3529$ and $\lambda=3519{\cdot}24$. The indium absorption spectrum behaves similarly with rise in temperature. The differences between the temperatures at which the respective lines of the $2p_2$ and the $2p_1$ series are first observed increase as the series, aluminium to thallium, is ascended; for indium, the temperature difference is 100—150°, and for thallium about 400°. An indium adsorption line is observed at $\lambda=2836{\cdot}90$ which is not included in the series schemes. From these absorption experiments, it is clear that the outermost electron in the aluminium series of elements follows an azimuthal two quantum orbit. W. E. G.

The Ultra-violet Absorption Spectra of Aniline and the Toluidines. F. W. KLINGSTEDT (*Compt. rend.*, 1923, **176**, 248—250).—Aniline in solution in hexane shows nine narrow bands between $\lambda=2991$ and 2704, and a broad band at $\lambda=2340$. The narrow bands are almost equidistant from one another. With respect to benzene, the absorption bands of aniline are displaced towards the red, and the intensity of absorption is about eight times greater. The absorption spectrum of aniline in solution in water, alcohol, or carbon tetrachloride is very different from the normal spectrum. In these solvents, the narrow bands are fused into one broad band. The absorption spectra of *o*- and *p*-toluidines are very different. The ortho has two broad bands, whilst the para has seven narrow bands and a broad band in the extreme ultra-violet. W. G.

The Absorption in the Ultra-violet of a Series of Derivatives of Camphor. A. HALLER and R. LUCAS (*Compt. rend.*, 1923, **176**, 45—49).—A study of the absorption spectra in the ultra-violet of the benzylidene-, anisylidene-, piperonylidene-

m-hydroxybenzylidene-, *m*-methoxybenzylidene-, *p*-tolylidene, and *m*-tolylidene-derivatives of camphor shows that all these compounds present a strong absorption band, the maxima of which vary with each compound. On the other hand, benzylcamphor and anisylcamphor do not give this absorption band. The curves for *m*-hydroxylbenzylidenecamphor and for *m*-methoxybenzylidene camphor are practically identical. The maximum of absorption in the compounds named above is displaced further towards the red as the substituent group is of greater weight. W. G.

The Ultra-violet Absorption Spectra of some Alkaloids of the *iso*Quinoline Group. Narcotine, Hydrastine, and Hydrocotarnine. PIERRE STEINER (*Compt. rend.*, 1923, **176**, 244—246).—The results obtained indicate that the ultra-violet absorption spectrum of narcotine is determined by the benzene nucleus of its molecule; the *iso*quinoline nucleus only displaces the absorption towards the red. For papaverine (cf. this vol., ii, 2), on the other hand, it is the *iso*quinoline nucleus, and not the benzene nucleus, which is the determining factor. The spectrum of hydrastine only differs from that of narcotine by a displacement of its maxima and minima towards the shorter wave-lengths and by small differences in the intensity of absorption. Hydrocotarnine, which contains a partly saturated *iso*quinoline nucleus, has a spectrum formed of a single band in the ultra-violet. According to the results tabulated, it should be possible to estimate spectrographically 0·07 mg. of narcotine or hydrastine in 2 c.c. of solvent. W. G.

Absorption Spectra of Pyrrole and its Derivatives. II. The Influence of Methyl Groups on the Absorption Spectra of Pyrrole and its Derivatives. G. KORSCHUN and (MME) C. ROLL (*Bull. Soc. chim.*, 1923, [iv], **33**, 55—67).—The absorption spectra of the ethyl esters of the following pyrrolecarboxylic acids were examined: 2 : 5-dimethyl-, 2 : 3 : 5-trimethyl-, 1 : 2 : 5-trimethyl-, and 1 : 2 : 3 : 5-tetramethyl-pyrrole-4-carboxylic acids, 2 : 5-dimethyl- and 2 : 3 : 5-trimethyl-1-aminopyrrole-4-carboxylic acids, 2 : 5-dimethyl- and 1 : 2 : 5-trimethyl-pyrrole-3 : 4-dicarboxylic acids, and 2 : 5-dimethyl- and 2 : 3 : 5-trimethyl-1-carbamidopyrrole-4-monocarboxylic acids, and also that of 1 : 2 : 5-trimethyl-pyrrole. The general conclusions drawn are that the introduction of a methyl group into position 1 (attached to nitrogen) causes a displacement of the absorption curve towards the ultra-violet. At the same time, if the derivative has two absorption bands they are united into one band. On the contrary, the introduction of methyl into position 3 causes a displacement of the curve towards the red, and at the same time the first band is lowered and the second raised. The methyl groups in positions 2 and 5 in 1 : 2 : 5-trimethylpyrrole displace the curve towards the red. Three methyl groups introduced into pyrrole in positions 1 : 2 : 5 only increase very slightly the intensity of the absorption bands. G. F. M.

Colour and Chemical Constitution. XVI. Further Miscellaneous Observations. JAMES MOIR (*Trans. Roy. Soc. S. Africa*, 1922, **10**, 233—237).—In this paper are given the absorption wave-lengths of all the "monocyclic" and "dicyclic" dyes which were used in establishing the author's theory of the colour of "cyclic" coloured substances (cf. A., 1921, ii, 6; 1922, ii, 333).

2 : 4′-Dihydroxybenzhydrol has λ 543 in alkali, λ 486 in hydrochloric acid, and λ 495 in water suspension. The 4 : 4′-isomeride has λ 539 in dilute alkali but in acid is the same as the 2 : 4′-compound. 2-Hydroxy-4′-dimethylaminobenzhydrol has λ 561 (broad) in alkali, λ 500 in acid; the 4 : 4′-compound has λ 572 in alkali and λ 504 in acid. 2 : 4 : 4′-Trihydroxybenzhydrol has λ 494 instead of the expected λ 550. 2 : 4-Dihydroxy-4′-methoxybenzhydrol has λ 380 in alkali and appears to be monocyclic; 2 : 4-dihydroxy-3′ : 4′-dimethoxybenzhydrol-2′-carboxylic acid is also monocyclic, with λ 390 in alkali, and so is mono-α-naphtholphthalein, from phthalaldehydic acid and α-naphthol, with λ 370. The C-phenyl derivative of the last-named has λ 401 in alkali, but λ 543 in strong sulphuric acid. The hydrol from *p*-hydroxybenzaldehyde and α-naphthol is violet with λ 590, whilst that from β-naphthol is pink, λ 556 in alkali. Phenol-β-naphtholphthalein has λ 570. The following show differences in sodium hydroxide (1) and sodium hydrogen carbonate (2), respectively: 3-hydroxyphenolphthalein λ 556 (1) and λ 562 (2); 3 : 6-dihydroxyphenolphthalein, λ 549 (1) and λ 563 (2); 4 : 5-dihydroxyphenolphthalein, λ 558 (1) and λ 568 (2). 5-Methoxyphenolphthalein has λ 565, whilst the 3 : 6-, 4 : 5-, and 5 : 6-dimethoxyphenolphthaleins have λ 568, λ 556, and λ 571, respectively. Other phenolphthalein derivatives examined were: 3-nitro-, λ 570; *a*-nitro-*fgjk*-tetrabromo-, λ 597 (cf. this vol., ii, 48, for nomenclature); 5-nitro-, λ 572; *abcd*-tetrachloro-, λ 581. Phenoldimethyl-α-naphthylaminephthalein is green, λ 625.

The following derivatives of Ghosh's quinolinic acid were examined: phenolquinolinein, λ 533; *o*-cresolquinolinein, λ 544; thymolquinolinein, λ 593; resorcinquinolinein, λ 490; orcinquinolinein, λ 496.

In the triphenylcarbinol series the following are given: *o*-hydroxymalachite-green, λ 627 neutral, λ 572 in alkali, λ 505 in acid; 2′-hydroxy-4-dimethylaminofuchsone, λ 490 neutral, λ 533 in alkali, λ 479 in acid; *p*-methoxymalachite-green, λ 605; *p*-methoxybenzaurine, λ 551; *p*-nitromalachite-green, λ 642; *p*-aminomalachite-green, λ 581 in acetic acid. Values are also given for a considerable number of unclassified coloured substances. E. H. R.

Cells with a Fluorescent Liquid. A. GRUMBACH (*Compt. rend.*, 1923, **176**, 88—90).—Goldmann (*Ann. Physik*, 1908, **27**, 449) has shown that when one of two electrodes plunged into a fluorescent liquid is illuminated an *E.M.F.* is set up and the illuminated electrode is positive. This was shown for saturated alcoholic solutions. It is now shown, working with dilute aqueous solutions, that the same effect may be obtained by keeping the

cell in the dark throughout and introducing into it near to one of the electrodes 1 c.c. of the same solution which has been intensely illuminated by a mercury arc for two hours. In this case, the electrode near to which the liquid is introduced is at first negative. The *E.M.F.* at first increases to a maximum and then decreases and finally changes its sign. With direct illumination of the electrode, it is found that the *E.M.F.* continues to increase for some time after the source of light has been removed. W. G.

Observations on the Phototropy of Inorganic Systems. José Rodríguez Mourelo (*Anal. Fis. Quim.*, 1922, **20**, 601—605; cf. A., 1922, ii, 604).—Further observations on the phototropy of sulphides of barium, strontium, and calcium.

G. W. R.

The Influence of Light on Zinc Sulphide. P. Lenard (*Ann. Physik*, 1923, [iv], **68**, 553—573).—The cause of the darkening of zinc sulphide phosphors has been traced to the polymerised sulphide molecules, which are effective in phosphorescence. The darkening occurs, however, in zinc sulphide, which is not phosphorescent, and it appears that the phenomenon has no direct relationship to the phosphorescence. The wave-lengths of the light producing darkening do not correspond with those effective in exciting phosphorescence. Water is necessary, and ozone, hydrogen peroxide, chlorine, etc., destroy the effect. On the other hand, ammonia or reducing agents like formaldehyde reactivate a phosphor which has lost its sensitivity to light. The alkaline earth and magnesium phosphors do not blacken. W. E. G.

Influence of Adsorption of Ions on the Photochemical Sensitiveness of Silver Bromide. K. Fajans and W. Frankenburger (*Z. Elektrochem.*, 1922, **28**, 499—505).—The authors have investigated the dependence of the sensitiveness of silver bromide on the method of precipitation. It is a known fact that silver bromide precipitated in the presence of an excess of silver nitrate is much more sensitive than that precipitated in the presence of an alkali halide. It is shown that under the influence of light the primary process taking place in silver bromide consists in the transference of an electron from a bromine-ion to a silver-ion with the formation of neutral atoms of bromine and silver. The work necessary to effect this change is dependent on the forces exerted on this electron in its initial and final states. In the presence of silver-ions from silver nitrate, these forces are smaller, and consequently the work required to effect the change is smaller, and the sensitiveness of the silver bromide is increased. J. F. S.

The Gamma Rays of the Family of Radium and of Thorium Studied by their Photoelectric Effect. M. de Broglie and J. Cabrera (*Compt. rend.*, 1923, **176**, 295—296; *Anal. Fis. Quim.*, 1922, **20**, 467—472).—By means of the apparatus previously described (A., 1922, ii, 330), results have been obtained which are in accord with those of Ellis (A., 1921, ii, 422; 1922, ii, 466) and Meitner (A., 1922, ii, 416). W. G.

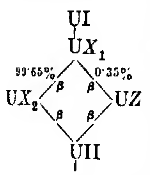
Röntgen Spectra and the Periodic System of the Elements. N. Bohr and D. Coster (*Z. Physik*, 1923, **12**, 342—374).—This paper, which forms a continuation of the Bohr theory of atomic structure (A., 1922, ii, 363), and papers by Coster (A., 1922, ii, 491, 677), examines the relationship between the Röntgen spectra, and the periodicity of the chemical properties, and the optical spectra of the elements. It is shown that the movements of the inner electrons are subject to the same laws which operate in the case of the valency electrons.

A table of the number of electrons in the various sub-groups of orbits is given for a large number of elements. This table, which is based on spectroscopic data, illustrates the building up of the electronic orbits with rising atomic number. The appearance of a new type of orbit is accompanied by a marked change in the chemical properties and the optical spectra of the elements. A new classification is proposed for the Röntgen spectra, in which the principal groups are divided into sub-groups, which are designated by Roman numerals, and to each level is given a value for n and k of the form $n(k_1,k_2)$ [for example, $2(2_1 2)L$ III]. As in the work of Coster (*loc. cit.*), an arrangement of the Röntgen spectra is put forward which is based on a relationship between the frequency ν of each line, and the difference between two spectral terms T' and T''. In agreement with the principles of the quantum theory of line spectra, these spectral terms, multiplied by h, give the energy required to transfer the electron from its normal orbit. The values T/R and $\sqrt{T/R}$ (where R is the Rydberg constant) are derived, and tabulated for the K, L, M, N, O, and P spectra, and where the experimental data are missing, the Röntgen spectra are interpolated from known values. Since the spectra are slightly affected by the form in which the element is excited, a little uncertainty is introduced into the values of some of the elements with low atomic numbers; also the fine structure of some of the lines is a source of error. $\sqrt{T/R}$ is plotted against the atomic number for all the Röntgen spectra available, and characteristic breaks are seen to occur in the curves for the L, M, N, and O spectra. The principal changes of slope occur in the neighbourhood of the platinum, the rare earth, and the iron groups. These irregularities are found at those atomic numbers where it is predicted that a new sub-group of electrons makes its appearance. The appearance of electrons in the 4_4 orbit at the element cerium, the commencement of the rare earth group, produces a sudden alteration in the slope of the $\sqrt{T/R}$ curve. At this point two of the lines in the M and N series separate into doublets. The binding energy of the 4_4 orbit, at atomic number 58 (cerium), is about the same as that of the 6-quantum orbit, and much less than that of the 5 and the 5_2 orbits. The energy of the 4_4 orbit increases as the atomic number rises, until after the rare earth family of elements it exceeds the energy of the 5-quantum orbits. This behaviour is of undoubted importance for the study of the chemical properties of the rare earth group. The changes in energy of the electronic orbits is more gradual at the end than at the beginning of this

group. The value of $\sqrt{T/R}$ for the O levels (5 quantum) changes very slightly between atomic numbers 58 and 72. This point is of great theoretical interest. The effective values of N and n for the O levels probably remain constant throughout the rare earth group. The constancy of N and n may also explain the similarity of the chemical properties and optical spectra of homologous elements, in spite of considerable changes in the principal quantum number of the outer electronic orbit. The lack of periodicity in the K and L series is accounted for by the suggestion that the effective values of N and n for these orbits differ only slightly from the atomic number and the principal quantum number. Two types of doublets occur in the Röntgen spectra. The curves for one type run parallel throughout the whole of their course, whereas for the other type they rapidly approach one another with decreasing atomic number.

Although there is no evidence of periodicity in the Röntgen spectra in the same sense as it occurs in the optical properties, it is expected that relationships will be obtained which will give a measure of the periodic behaviour of the elements. W. E. G.

Uranium-*Z* and its Parent Substance. OTTO HAHN (*Z. physikal. Chem.*, 1923, **103**, 461—480).—A method is described for the determination of the relation of the activity of uranium-Z to that of uranium-X; the method has been applied to a large number of uranium-X preparations of different ages and a satisfactory constant value for the relationship obtained. The constancy of the value allows the conclusion to be drawn that uranium-X_1 is the parent substance of uranium-Z. Uranium-X_1 therefore undergoes a dual β-ray disintegration, of a kind which has hitherto not been observed with radioactive elements. A new method for detecting uranium-Z is described. From the activity ratio uranium-Z : uranium-X, it is shown that the branching relationship is about 0·35%. In the calculation of this figure, the absorption of the β-radiation of uranium-Z with reference to that of uranium-X_1 and uranium-X_2 is taken into account. The disintegration scheme of the earlier members of the uranium series is therefore most probably represented by the annexed scheme. J. F. S.



Ionisation by Collision of Hydrogen, Nitrogen, and Argon. T. L. R. AYRES (*Phil. Mag.*, 1923, [vi], 45, 353—368).—The ionisation of hydrogen, nitrogen, and argon molecules on collision with electrons has been measured for comparatively small values of the ratio of electric force, X, to the gas pressure p. The range examined is from $X/p=1$ to $X/p=600$, and over part of this range Townsend and Bailey (cf. A., 1922, ii, 836) have recently measured the velocity in the direction of the electric force, and the mean velocity of agitation of the electrons in these gases. Ionisation by the electrons occurred for values of X/p as low as 2 in argon, 5 in hydrogen, and 10 in nitrogen. The effect of positive

ions was observed down to $X/p=10$ for argon, 30 for hydrogen, and 100 for nitrogen. No evidence was obtained for any appreciable variation in the ionisation due to slight contamination of the hydrogen and nitrogen, but small amounts of impurities in the argon caused a marked diminution of the ionisation, and increased the sparking potential. The ionisation with both positive and negative ions is in general agreement with that found by Townsend and Hurst for hydrogen and nitrogen (cf. A., 1906, ii, 262). For argon, however, at low values of X/p, the ionisation is greater than found by earlier investigators. The nature of the metal used as electrodes is without appreciable effect on the ionisation.

W. E. G.

Thermal Ionisation of Gaseous Elements at High Temperatures. ARTHUR A. NOYES and H. A. WILSON (*J. Amer. Chem. Soc.*, 1922, **44**, 2806—2815).—A theoretical paper in which the thermodynamic equation used by Saha (A., 1920, ii, 659) for calculating the thermal ionisation of the neutral atoms of gaseous elements into positive ions and electrons from their ionisation potentials is discussed with reference to the assumptions involved in the calculation. It is shown that the recent measurements of H. A. Wilson (A., 1916, ii, 72), as well as the earlier experiments of Arrhenius (A., 1891, 5, 575), on the electrical conductivity of flames into which salt solutions are sprayed clearly indicate that the conduction arises from an ionisation process of the type under consideration, and that they make possible a computation of the relative magnitudes of the ionisation constants. It is also shown that the relative ionisation constants of the five alkali elements, calculated on the one hand from the conductivity of flames and on the other from the ionisation potentials by the thermodynamic equation, form two series of values which run closely parallel to each other. Thus, although in passing from lithium to cæsium the ionisation constant increases 5700 times, the ratio of the constants derived by the two methods for any one element does not differ from the mean value of that ratio for all five elements by more than 40%. The absolute values of the ionisation constants are derived from the flame conductivities with the aid of previous rough determinations of the mobility of the electrons and of the number of them per c.c. in similar flames. Although this could only furnish an estimate of the order of magnitude of the constants, yet they were found to correspond well with the values calculated by the thermodynamic equation, the latter being only 1·1 to 2·3 times as large.

J. F. S.

The Ionisation of Mercury Vapour in Presence of Argon. GEORGES DÉJARDIN (*Compt. rend.*, 1922, **175**, 1203—1206; cf. this vol., ii, 47).—Experiments were made with mercury vapour in presence of argon in order to ascertain whether the effect of the gas is similar to that of helium. The results show that ionisation resulting from impacts on mercury atoms of electrons the speed of which is greater than the critical ionisation speed (corresponding with 10·4 volts) is inappreciable and only becomes evident at a

speed corresponding with 11·3 volts. On increasing the potential, a sudden increase in the current is observed when the spatial charge of the electrons is completely neutralised and simultaneously a glow appears in the neighbourhood of the electrodes. The corresponding potential (the "illumination potential") depends on the shape of the electrodes and on the pressure. Ionisation of the argon by direct impact begins at a potential of about 15 volts. Between 11·3 volts and the illumination potential the intense lines of the mercury arc spectrum are obtained; above this limit the whole mercury arc spectrum and the red spectrum of argon are visible, the latter increasing in intensity above 15 volts. Above 35 volts, lines in the blue spectrum of argon are observed. The author infers from his results that for electrons traversing an atmosphere of argon there exists a first critical velocity of about 11·3 volts and that a resonance radiation emitted by the gas under these conditions ionises mercury vapour. This ionisation is not accompanied by any notable modification of the mercury spectrum analogous to that produced in presence of helium. Argon appears to exert only a feeble selective action on the second spectrum of hydrogen (Merton and Barratt, A., 1922, ii, 461) and on the cadmium spectrum (Collie and Watson, A., 1918, ii, 383). It is possible that the special influence of helium is due to the greater quantum of the radiations which it emits. H. J. E.

Ionisation Produced by the Hydration of Quinine Sulphate. (MLLE) CHAMIÉ (*Compt. rend.*, 1923, **176**, 251—253).—When the hydration is carried out in an ionisation chamber and the curve of increase in weight is compared with the curve of the diminution in current, it is found that the duration of the phenomenon is the same for the two curves and depends on the density of the layer of the salt. Any effect which modifies the one curve modifies the other in the same manner. The weight of water of hydration as well as the maximum intensity of the current of ionisation and the quantity of electricity liberated during the hydration appear to be proportional to the weight of quinine sulphate used.

W. G.

Conduction Process in Ordinary Soda-Lime Glass. CHARLES A. KRAUS and EDWARD H. DARBY (*J. Amer. Chem. Soc.*, 1922, **44**, 2783—2797).—The replacement of sodium-ions in soda-lime glasses by ions of other metals has been investigated. It is shown that although the sodium-ions may be replaced by the ions of many other metals from their amalgams as well as from their fused salts, under a potential gradient, replacement occurs more readily from the fused salts than from the amalgams. In most instances, the glass formed on replacement is not stable. In some cases, the glass is completely disintegrated and in others it cracks on cooling. Sodium may be replaced by silver to a depth of about 0·1 mm. without cracking the glass. On replacing sodium by silver under the action of a potential, a sharp boundary is formed between the sodium and the silver ions. From the rate of motion of the boundary, the speed of the ions under a unit potential gradient

has been determined; the following values are recorded: 278°, 4.52×10^{-8}; 295°, 1.46×10^{-7}; 323°, 3.26×10^{-7}, and 343°, 5.9×10^{-6} cm./sec. The increased velocity of the ions with increased temperature corresponds with the increased conductivity of the glass with increased temperature. The fraction of the total sodium present in the glass, which takes part in the electrical conduction, has been calculated from the depth of penetration of the boundary and from the amount of electricity passing, as well as from the change in weight of the tube. It is found that 74—82% of the total sodium present in an ordinary soda-lime glass takes part in the conduction. The remaining sodium is either not in a charged state or otherwise the ions are held in fixed positions. The fraction ionised, as defined in this way, increases slightly between 278° and 343°. The following values of the percentage ionisation and the resistance in ohms are recorded: 278°, 74·4%, 72800 ohms; 295°, 76·8%, 35000 ohms; 323°, 79·4%, 14200 and 343°, 81·0%, 6600 ohms. J. F. S.

Potential Difference between Glass and Electrolytes in Contact with Glass. WALTER S. HUGHES (*J. Amer. Chem. Soc.*, 1922, **44**, 2860—2867).—The potential difference between glass and solutions of electrolytes has been investigated at 25°. It is shown that glass surface potentials are established and maintained by the passage of electricity through glass. The glass surface potential is a linear function of the hydrogen electrode only over a limited range of values. Variations in the glass surface potential may be used as the basis of an electrometric titration method in the presence of oxidising agents which render the hydrogen electrode useless for such purposes. In such cases, the method might yield data which could not be obtained in any other way. The presence of certain substances, other than hydrogen-ions, such as concentrated solutions of salts or gelatin, affects glass surface potentials. J. F. S.

Significance of the Electrode Potential. JAROSLAV HEYROVSKÝ (*Proc. Roy. Soc.*, 1923, [*A*], **102**, 628—640).—Evidence is adduced that the process by which a metallic electrode, immersed in an aqueous solution, becomes charged is represented by $M + OH' \longrightarrow MOH + \ominus$. By the application of the electronic conception of chemical combination to a reversible thermodynamic cycle, a formula is obtained for the electrode potential in terms of the ionisation potential and basigenity of the metal. The basicity of metallic oxides is discussed by means of Beketoff's principle (A., 1889, 332), and it is concluded that a metallic hydroxide is the more basic the more negative the electrode potential and the greater the equivalent weight of the metal. The mechanisms of galvanic and concentration cells, the phenomena of electrodeposition and overvoltage, and electrode processes in non-aqueous solvents are discussed in the light of the theory developed. "Absolute zero potential" values of contact *E.M.F.* derived from electrocapillary phenomena are shown to be illusory,

and the probable potential at which reversal of the sign of the charges in the double layer occurs is indicated. J. S. G. T.

Determination of Absolute Single Electrode Potentials. ALLEN GARRISON (*J. Amer. Chem. Soc.*, 1923, **45**, 37—44).—The methods hitherto employed for determining absolute single electrode potential differences have been enumerated and briefly discussed and a new method of effecting this determination is described. The method is based on the assumptions, (1) that the mechanical force on a substance suspended in an electrolyte through which an electric force acts is due to the charge on the suspended system, (2) that the direction of the force is determined by the sign of the charge, and (3) that there is no charge or potential difference relative to the electrolyte when, in an electric field, there is no mechanical force relative to the electrolyte. The method used consists in suspending a light metal needle, shaped like the needle of a quadrant electrometer, by a phosphor-bronze ribbon in an electrolyte containing such a concentration of the metal-ion that there is no electric double layer at their interface. This isoelectric condition is indicated by the absence of any mechanical forces when an electric field is applied through the electrolyte. The potential of the needle is at the same time compared with the potential of a standard half cell. On eliminating the liquid junction potential the measured *E.M.F.* is the absolute potential of the constant electrode. A full description of the apparatus and its method of use is given in the paper. Using a silver needle at its isoelectric point as the zero electrode, the absolute potential of a $0{\cdot}1N$-calomel electrode is found to be between $-0{\cdot}20$ volt and $-0{\cdot}10$ volt at 25°. This result is a confirmation of Billitzer's value of $-0{\cdot}13$ volt, and it removes the objections which have been made to the method employed by Billitzer (*Z. Elektrochem.*, 1902, 8, 638). J. F. S.

The Polarisation of Electrodes. J. E. VERSCHAFFELT (*Rec. trav. chim.*, 1922, **41**, 764—777; cf. Aten, A., 1916, ii, 370).—A mathematical argument in which the author develops views previously put forward (*Bull. Acad. roy. Belg.*, 1919, 441). The conclusion is drawn that the variation of potential due to the application of *E.M.F.* is mainly effective at the cathode in the case of two electrodes of a metal in contact with a solution of one of its own salts, whilst with the same salt but with electrodes of a more electropositive metal the anode potential undergoes the greater variation and thus only the anode is polarised. H. J. E.

Activity Coefficient of Hydrochloric Acid in Aqueous Salt Solutions. HERBERT S. HARNED and NORMAN J. BRUMBAUGH (*J. Amer. Chem. Soc.*, 1922, **44**, 2729—2748).—*E.M.F.* measurements of cells of the following types have been carried out at the temperatures indicated: $H_2|MCl_2$ (c) in $0{\cdot}1N$ $HCl|HgCl|Hg$ at 18°, 25°, and 30°, where M denotes barium, strontium, or calcium; $H_2|MCl_2$ in $0{\cdot}1N$ $HCl|KCl$ (sat.)$|HgCl|Hg$ at 25°, where M signifies the same metal as before; $H_2|KCl$ (c) in HCl $(c')|AgCl|Ag$, and $H_2|KCl$ (c) in HCl $(c')|HgCl|Hg$, where c' is $0{\cdot}01N$ and $0{\cdot}001N$, at

18°, 25°, and 30°. From the data obtained, the decrease of free energy and the decrease of the heat content of the cell reaction have been calculated, as well as the changes in partial molecular free energy and heat content of hydrochloric acid in the mixtures. The mean activity coefficients of hydrochloric acid in solutions of potassium, sodium, lithium, barium, calcium, and strontium chlorides have also been calculated. By means of the formula $\log F_a' = \alpha' c_1 - \beta' \mu^{m'} + \alpha'' (\mu - c_1)$, the values of the mean activity coefficients (F_a') of hydrochloric acid in the acid salt mixtures, containing acid at concentrations from $0{\cdot}001N$ to N, may be calculated with considerable accuracy. In solutions of greater dilution of acid, it is necessary to add a term to the above equation which is a function of the salt to acid concentration ratio, thus: $\log F_a' = \alpha' c_1 - \beta' \mu^{m'} + \alpha'' (\mu - c_1) + \gamma' [(\mu - c_1)/c_1]$ is approximately valid for solutions containing acid of concentration as low as $0{\cdot}001N$. Thus when $(\mu - c_1)/c_1$ is very high, a considerable increase in the value of F_a' is observed. In the above equations c_1 is the concentration of acid, α', β', α'', m' are constants, and μ is the ionic strength and for uni-univalent electrolytes equals the sum of the concentrations of the salt and acid or $(c + c_1)$. It is pointed out that the effect mentioned above is probably due to an increase in activity of the hydrogen-ion. If, as is to be expected, the same phenomenon is observed in mixtures containing other ions, it will be of considerable importance, especially in dealing with the problem of the solubility of sparingly soluble salts in solutions of other salts. Evidence has been obtained which leads to the conclusion that in solutions of strong bivalent chlorides, at the same temperature and concentration, the chloride-ion will have the same activity, and also that the activity of the chloride-ion in uni-univalent chloride solutions is greater than in bivalent chloride solutions of the same ionic strength. J. F. S.

Activities of the Ions of Potassium Hydroxide in Aqueous Solution. M. KNOBEL (*J. Amer. Chem. Soc.*, 1923, **45**, 70—76).—The author has determined the *E.M.F.* of cells of the type $H_2|KOH\ (c_1)|KHg_x|KHg_x|KOH\ (c_2)|H_2$ at 25° for concentrations of potassium hydroxide ranging from $3N$ to $0{\cdot}0001N$. The activity coefficients of the ions of the solution at various concentrations and the free energy of dilution between various concentrations have been calculated and tabulated. The data given by Chow (A., 1920, ii, 281) are found to be incorrect; differences of 2—8% are found between Chow's values and the present values. The relationship between the activity and concentration for potassium hydroxide has been found to be similar to that for other uni-univalent electrolytes. J. F. S.

Degree of Ionisation of Ethyl Alcohol. I. From Measurements of Conductivity. PHILIP S. DANNER and JOEL H. HILDEBRAND (*J. Amer. Chem. Soc.*, 1922, **44**, 2824—2831).—The methods available for the purification of ethyl alcohol are discussed as to their efficiency, and the following method has been adopted for the preparation of absolutely pure material. Commercial 95% alcohol

was distilled with 5 c.c. of concentrated sulphuric acid and 20 c.c. of water per litre and the distillate boiled for several hours with 10 g. of silver nitrate and 1 g. of potassium hydroxide per litre. This product was distilled on to commercial quicklime, 600—700 g. per litre and boiled for eight hours. The mixture was then shaken vigorously for twenty-four to thirty-six hours at the ordinary temperature and distilled on to specially prepared quicklime, made by burning the mixture of calcium hydroxide and carbonate such as is obtained by drying slaked lime in the air. This product was present in the quantity 100—150 g. per litre of alcohol and the mixture was boiled for four to six hours. The alcohol was then distilled into the vessel from which the final purification was to be made and at this stage had a specific conductivity $1 \cdot 0 \times 10^{-7}$ $ohms^{-1}$. Subsequent distillation in evacuated sealed apparatus gave a value $2 \cdot 2 \times 10^{-8}$ $ohms^{-1}$, but here the most volatile portion was not removed. Repeated vacuum distillation with removal of the most volatile portion gave a steadily decreasing value with each repetition until the tenth distillation gave the value $1 \cdot 35 \times 10^{-9}$ $ohms^{-1}$, and this is regarded as the value for the purest ethyl alcohol. The dissociation constant calculated from this figure is $2 \cdot 89 \times 10^{-16}$ for the ionisation $C_2H_5{\cdot}OH \rightleftharpoons C_2H_5O' + H^{\cdot}$; the molecular fraction ionised is $1 \cdot 0 \times 10^{-9}$, which is comparable with the similar value for water, $1 \cdot 8 \times 10^{-9}$. J. F. S.

Degree of Ionisation of Ethyl Alcohol. II. From Measurements of Electromotive Force. PHILIP S. DANNER (*J. Amer. Chem. Soc.*, 1922, **44**, 2832—2841; cf. preceding abstract).—The *E.M.F.* of a series of cells of the types $H_2Pt|HCl,HgCl|Hg$, $Hg|HgCl,NaCl|Na$ (2-phase amalgam), and Na (2-phase amalgam)$|C_2H_5{\cdot}ONa|PtH_2$, all in pure ethyl alcohol (*loc. cit.*) have been measured at 25°. The cells were very slow in reaching an equilibrium value, but were reproducible to 0·0001 volt, and calculations based on the values obtained involve no assumptions as to the value of the potential at the boundary water/alcohol, since this is not present. The dissociation constant for the ionisation $C_2H_5{\cdot}OH \rightleftharpoons C_2H_5O' + H^{\cdot}$ is calculated to $7 \cdot 28 \times 10^{-20}$ and the molecular fraction dissociated to $1 \cdot 6 \times 10^{-11}$. This indicates that ethyl alcohol is dissociated only to 1/100 of the amount to which water is dissociated. The discrepancy between the present results and those given in the previous paper (*loc. cit.*) is attributed to the assumptions involved in the interpretation of the conductivity measurements, since the maximum possible error of the *E.M.F.* measurements, 0·002 volt, would not produce a greater error than 10% in the value of the dissociation constant. J. F. S.

The Ionisation of Water in Solutions of Electrolytes. E. DOUMER (*Bull. Soc. chim.*, 1923, [iv], **33**, 49—55).—Hittorf's assumption that water is only ionised in negligible proportions in solutions of electrolytes does not seem to be justified, especially in the case of acid electrolytes, and particularly of hydrochloric acid solutions. Evidence for the fact that the liberation of oxygen at the anode in the electrolysis of hydrochloric acid is a primary

effect, and not a secondary reaction due to the action of nascent chlorine on water, is furnished by electrolysis with a silver or mercury anode, when the amount of oxygen liberated is actually greater than with platinum anodes, whilst all the chlorine combines with the anode forming the metallic chloride. Initially the silver anode becomes covered with a brown film, which eventually becomes white, so that both chlorine and oxygen are apparently discharged simultaneously, the former then displacing oxygen from the oxide when free metal is no longer available on the surface of the anode. Experiments on the electrolysis of dilute hydrochloric acid showed that for 50 c.c. of hydrogen liberated at the cathode 16·55 c.c. of oxygen were formed at the anode, and it is therefore concluded that of the total hydrogen-ions discharged $2\times16\cdot55/50$ were derived from ionised water, that is, about 66%. This surprisingly high proportion finds confirmation in a determination of the total loss of hydrochloric acid in the electrolyte compared with the theoretical loss had all the liberated hydrogen been derived from hydrogen chloride. Further, the molecular conductivity of hydrochloric acid solutions is about three times as great as that of alkali chloride solutions, and the explanation provided by the above hypothesis is that in such acid solutions there are in addition to hydrogen- and chlorine-ions about twice as many hydrogen- and hydroxyl-ions. G. F. M.

Theory of the Polarisation of the Electrolytic Generation of Oxygen. II. Anodic Behaviour of Manganese in Solutions of Alkali Hydroxides. G. Grube and H. Metzger (*Z. Elektrochem.*, 1923, **29**, 17—30; cf. *ibid.*, 1922, **28**, 568).—The anodic behaviour of pure manganese in solutions of sodium hydroxide has been investigated. It is shown that in hot concentrated solutions with small current densities, manganese passes into solution in the bivalent condition, with medium current densities (0·3—0·1 amp./dcm.^{2}) in the tervalent condition, and with higher current densities in the sexavalent condition. The solution of manganous oxide thus produced is yellowish-red in colour, and that of the manganic oxide brownish-red. The sexavalent manganese forms manganate, the production of which is always accompanied by the liberation of oxygen. At ordinary temperatures and also in dilute hydroxide solution, manganese passes into solution in the septavalent condition, with liberation of oxygen. The potentials corresponding with the individual anode changes have been measured at various temperatures and concentrations of alkali. The polarisation of the electrolytic evolution of oxygen occurs because the manganese becomes covered with a thin film of dioxide which then forms permanganic acid according to the equation $MnO_2+2H_2O+3\oplus \longrightarrow MnO_4'+H^{\cdot}$. This substance then decomposes completely at lower current densities in N-sodium hydroxide with the evolution of oxygen according to the equation $2HMnO_4 \longrightarrow 2MnO_2+H_2O+3/2O_2$; at higher current densities only a portion decomposes in this way, whilst the other portion diffuses into the solution and forms sodium permanganate. The competition of the velocity

of the two reactions, the oxidation of manganese dioxide to permanganate, and the spontaneous decomposition of the permanganic acid with liberation of oxygen, determines the extent to which the current is used for the liberation of oxygen and the formation of permanganate and also the potential of the process. J. F. S.

Effect of Fluorine on Electrolytic Oxidations. A. Ríus y Miró (*Anal. Fís. Quím.*, 1922, **20**, 644—661).—The electrolytic oxidation of chrome alum and potassium hydrogen phosphate is increased with increasing amounts of potassium fluoride. It is supposed that the fluoride-ions at the moment of their discharge at the anode react directly, or indirectly by means of a peroxide of platinum, with the electrolyte present. With water, ozone is formed, whilst in other cases per-compounds may be formed, for example, in the case of phosphates, perphosphoric acid. The theoretical objections to this theory are discussed. G. W. R.

Electrolysis with a Dropping Mercury Cathode. I. Deposition of Alkali and Alkaline-earth Metals. Jaroslav Heyrovský (*Phil. Mag.*, 1923, [vi], **45**, 303—315).—The decomposition potentials of the alkali and alkaline-earth metals have been determined by means of a dropping mercury cathode. When the dropping electrode is made the cathode, it is found that in neutral or alkaline solution hydrogen is not evolved even with high polarisations, and hence this arrangement is convenient for the study of the cathodic deposition of the most positive metals, which are otherwise attacked by water. The decomposition potentials found by this method were: lithium $-2\cdot023$, potassium $-1\cdot883$, sodium $-1\cdot860$, cæsium $-1\cdot837$, rubidium $-1\cdot796$, ammonium $-1\cdot787$, calcium $-2\cdot023$, magnesium $-1\cdot903$, strontium $-1\cdot862$, and barium $-1\cdot814$ volts. Assuming that the alkali metals form compounds with the mercury, it is possible to calculate the affinity of the metal for mercury, this being given by the equation $A = \pi_n - E.P.$, where π_n is the observed decomposition potential with the drop electrode, and *E.P.* is the decomposition potential obtained by G. N. Lewis. The affinity for mercury increases with increasing atomic weight, but sodium occupies an anomalous position, behaving like a more noble metal. It is deduced that the *E.P.* of cæsium is $-3\cdot3$ volt. W. E. G.

Transport Numbers of Potassium Hydroxide in Aqueous Solution. M. Knobel, D. K. Worcester, and F. B. Briggs (*J. Amer. Chem. Soc.*, 1923, **45**, 77—79).—The *E.M.F.* of concentration cells of potassium hydroxide of the type $H_2|KOH(c_1)|KOH(c_2)|H_2$ have been measured at 25°, for concentrations between $3\cdot0N$ and $0\cdot01N$. These values, combined with those obtained for cells without transport (see this vol., ii, 116) have been used to calculate the transport number of the potassium-ion in solutions of potassium hydroxide of various concentrations. The transport number of the potassium-ion is found to be constant and equal to 0·2633 over the whole range of concentration $3\cdot0N$ to $0\cdot01N$, and to increase with decrease in concentration below this value to

0·274 at infinite dilution. The following values of the *E.M.F.* are recorded for the cells measured: $c_1=3{\cdot}0N$, $c_2=0{\cdot}3N$, $\epsilon=0{\cdot}03683\pm0{\cdot}00003$; $c_1=1{\cdot}0N$, $c_2=0{\cdot}1N$, $\epsilon=0{\cdot}03104\pm0{\cdot}00003$; $c_1=0{\cdot}3N$, $c_2=0{\cdot}1N$, $\epsilon=0{\cdot}01424\pm0{\cdot}00003$; $c_1=0{\cdot}3N$, $c_2=0{\cdot}03N$, $\epsilon=0{\cdot}02916\pm0{\cdot}00003$; $c_1=0{\cdot}1N$, $c_2=0{\cdot}01N$, $\epsilon=0{\cdot}03465\pm0{\cdot}00015$. J. F. S.

Possibility of Varying Intermediate Stages in the Kolbe Reaction and a Case of Anodic Ester Formation with Aromatic Acids. C. SCHALL (*Z. Elektrochem.*, 1922, **28**, 506–511).—The electrolysis of molten lead acetate, manganous acetate in benzoic acid, and alkali benzoates in benzoic acetate has been investigated; it is shown that in the case of metals of constant valency the change takes place according to the equation $x\mathrm{RCO_2}'+xF=x/2R\,.\,R+x\mathrm{CO_2}$, but when the metal has a variable valency the primary change is represented by the equation $\mathrm{M(RCO_2)}_x+x\mathrm{RCO_2}'+xF=\mathrm{M(RCO_2)}_{2x}$, and if the temperature is sufficiently high this reaction is followed by a secondary thermal action $\mathrm{M(RCO_2)}_{2x}=\mathrm{M(RCO_2)}_x+x/2\mathrm{R}\,.\,\mathrm{R}+x\mathrm{CO_2}$. These equations indicate that intermediate compounds may be formed in the Kolbe reaction. When potassium benzoate containing benzoic acid is electrolysed, using a silver anode, phenyl benzoate is produced. This formation is due, at least in part, to the oxidation of the acid to phenol by the silver oxide produced on the anode. J. F. S.

The Anomalies of Strong Electrolytes with Special Reference to the Theories of J. C. Ghosh. II. HENRY J. S. SAND (*Phil. Mag.*, 1923, [vi], **45**, 281—292; cf. this vol., ii, 55).—Alterations have been made in the subsidiary hypotheses of Ghosh, to bring them into line with the equation $\mu/\mu_\infty=e^{-G/NRT}$, where μ/μ_∞ is the ratio of the molecular conductivities and G the work required to separate one gram-mol. of ions. Although the theory is strengthened by these changes, the number of subsidiary hypotheses is so great that the above equation must be regarded as an empirical formula. The hindrances to conduction in a medium of uniform dielectric constant, by the electric fields of the ions, is of the nature of polarisation, and the conductivity should be greater with rapidly alternating currents and high potential gradients than with small, constant potential gradients. Since this conclusion is contrary to experiment, the idea of a solvent with uniform dielectric constant has been abandoned.

An explanation of ionisation is put forward based on the assumption that solvent molecules possess polar properties, the ionising media consisting of a number of bipoles, similar to those postulated by Debye in his explanation of the dielectric properties of the media. These bipoles, which are capable of rotation, are held when in the powerful electric field of the ion, and their rotation stopped and converted into vibrational motion. Each ion will thus consist of the simple charged atom or group in the centre of a number of polar water molecules, which is capable as a whole of rotatory or vibratory motion. The ions become bound when they meet other ions of different polarity, and are then only capable of vibration around a position of equilibrium and become incapable of

transmitting a current. These views lead to a formula similar to that of Ghosh. The Ghosh equation, whilst yielding satisfactory values for binary electrolytes, breaks down for salts like barium chloride. The introduction of the Milner virial into Ghosh's formulæ does not lead to any improvement. W. E. G.

Faraday's Law and the Action of the Electrical Discharge on Gases. A. DE HEMPTINNE (*Bull. Acad. roy. Belg.*, 1919, [v], 5, 521—527).—Faraday's law has been shown to hold, with fair approximation, for chemical effects produced by an electrical discharge on gases at low pressures. E. E. T.

Faraday's Law and the Chemical Action of the Electrical Discharge. A. DE HEMPTINNE (*Bull. Acad. roy. Belg.*, 1919, [v], 5, 161—177).—An investigation of the reduction of unsaturated oils by hydrogen, under the influence of an electrical discharge, the amount of reduction being followed by the change in iodine number of the oil. A large number of experiments, involving variations in thickness of dielectric, density of current, potential difference, etc., are described, and do not lend themselves to abbreviated description. The author concludes that Faraday's Laws of Electrolysis are obeyed, at any rate, roughly. E. E. T.

Faraday's Law and the Action of the Electrical Discharge on Metallic Oxides. II. III. IV. V. A. DE HEMPTINNE (*Bull. Acad. roy. Belg.*, 1919, [v], 5, 249—260; 1921, [v], 7, 146—155, 458—468, 590—595).—II. A study of the reduction of metallic oxides by hydrogen in presence of an electrical discharge. The results fall in line with those previously obtained with unsaturated oils (cf. preceding abstract). Lead peroxide is taken as a standard substance for reduction, and a large number of other metallic oxides and also chlorides and miscellaneous substances are compared with it. Carbon monoxide was found to be roughly as effective in reduction as hydrogen, the experiments being carried out at low pressures to avoid polymerisation, etc., of the monoxide.

III. The reduction of various substances by this method shows that, as a rule, it is unimportant whether the substance in question is in contact with the positive or with the negative electrode. Values are found for the ratio N/N', where N is the number of hydrogen molecules disappearing during a reduction and N' the number of ions and electrons (calculated from the measured current). This ratio has a value ranging from zero in the case of difficultly reduced oxides such as zinc or magnesium to above unity in the case of lead peroxide and manganese dioxide, etc., the reducibility of an oxide being connected with the electrolytic potential of the corresponding metal. Potassium chlorate is almost unaffected under conditions sufficing for the reduction of most oxides, a fact which is attributed to the purely electrical nature of the process, no thermal effect being produced by the incidence of positive ions or electrons. Thus, in the case of oxides, the amount of reduction is approximately proportional to the amount of current passing.

IV. The reduction of lead peroxide, cupric oxide, and ferrosoferric oxide is effected in a dried atmosphere of hydrogen by

means of an electrical discharge, the oxide in question being placed in contact with one of the electrodes. By measuring the variation of pressure, of potential difference between the electrodes, and the current flowing, a relation is found between the number (N) of hydrogen molecules used in the reduction and the number of positive ions (N_i) and electrons (N_e). The point is raised as to whether in ionisation the hydrogen molecule loses one or two electrons. Activated hydrogen (H_3) offers another explanation, but the mechanism of the reduction remains in doubt. With lead peroxide in contact with the positive electrode, N/N_e has values from 0 to 1·1, and when in contact with the negative electrode, values of 2·7 to 1·4 for N/N_i are obtained. Similar results are obtained for other oxides. If the positive ions are formed by the loss of one electron from each hydrogen molecule, and if each electron liberates one atom of oxygen, which then combines with one molecule of hydrogen, N/N_i and N/N_e should be equal to unity. Values (for these ratios) of 0·5 will correspond with the loss of two electrons when hydrogen is ionised and so on.

V. In the earlier sections the loss of weight of oxides when submitted to the action of an electrical discharge in presence of hydrogen was not determined. It is now found that, in the reduction of lead peroxide, the weight of hydrogen absorbed (as measured by the diminution in pressure) is equivalent to the loss in weight of oxide, whether the latter is in contact with the positive or with the negative electrode. The oxide formed as a result of the reduction is probably lead suboxide. When nitrogen is substituted for hydrogen in these experiments, no change is observed in either gas or solid, except such as could be accounted for owing to defects in the apparatus. Carbon monoxide, under similar conditions, causes the lead peroxide to gain in weight, probably owing to the formation of a deposit of a lower oxide of carbon. E. E. T.

Dissociation of Carbon in the Intensive Arc. LOUIS BELL and P. R. BASSETT (*Science*, 1922, **56**, 512).—In the spectrum of the "negative tongue" which appears in the carbon arc at currents of at least 100 amperes, there were found fifteen lines, of which seven were coincident with the most conspicuous helium lines, and two others with H_α and H_β. Some carbon nuclei are considered to dissociate into helium, and possibly further, although the hydrogen lines may be due to water vapour absorbed by the carbon.

CHEMICAL ABSTRACTS.

The Evolution of the Molecule of Ferric Hydroxide in Contact with Water. (MLLE) S. VEIL (*Compt. rend.*, 1923, **176**, 101—103).—The molecular coefficient of magnetisation, with reference to iron content, of the hydroxide and the oxide of iron depend, to a large extent, on the previous states through which the material has passed and the temperatures to which it has been heated. W. G.

The Calculation of the Magneton Number of an Atom in Solution. J. H. SMITH (*Phil. Mag.*, 1923, [vi], **45**, 375—378).—The magnetic susceptibility of cobalt chloride in water is greater

than in alcoholic solutions, and this change is associated with a shift in the maximum of the light adsorption from 0·510μ to 0·65μ. Making the assumption that Wiedemann's law of the additivity of magnetic susceptibility holds for solutions, the magneton number of the cobalt-ion in aqueous solution is found to be 24·6. The difference between the magnetic susceptibility in water and in alcoholic solutions may be ascribed either to a change in the diamagnetic or the paramagnetic part of the atom. A reasonable conclusion is that the frequency of the paramagnetic part of the atom is diminished, and this view is supported by the decrease in the frequency of the light absorbers in the atom.

W. E. G.

Paramagnetism and the Structure of the Atom. B. CABRERA (*J. Phys. Radium*, 1922, 3, 443—460).—The property of paramagnetism is confined very largely to the elements in column VIII of the Mendeléev classification and to the rare earths. The magnetic susceptibilities of the elements from chromium to copper, following the order of the atomic numbers, have been seriously studied, and data are available to fix the magneton number (Weiss) of the metallic ions for many of the elements in their various stages of oxidation. For these elements, the Weiss magneton number is seen to be given by a series of whole numbers, which are independent of the degree of ionisation of the salt. A theoretical interpretation of this regularity in the Weiss magneton number is sought in the structure of the atom, and, in particular, in the N-level of electrons. This level is subdivided into N_1 and N_2 levels, the latter first making its appearance with titanium. The number of electrons in the N_1 level augments from Ti$^{\cdot\cdot\cdot\cdot}$ to Cu$^{\cdot}$, for which element it attains a maximum value. It is assumed that the number of electrons in the M level remains constant at 8 throughout. On plotting the magneton number of the ion against the number of electrons in the N_1 level, a symmetrical curve is obtained giving a maximum at Fe$^{\cdot\cdot\cdot}$, when the magneton number is 29, and $N_1 = 5$. Ions containing an identical number of electrons in the N_1 level give the same magneton numbers; thus Fe$^{\cdot\cdot\cdot}$, Mn$^{\cdot\cdot}$, Mn$^{\cdot\cdot\cdot}$, and Cr$^{\cdot\cdot}$ give the same values. The points corresponding with Co$^{\cdot\cdot}$ and Fe$^{\cdot\cdot}$ are somewhat displaced, but these elements give a variable magneton number. At Ti$^{\cdot\cdot\cdot\cdot}$ and Cu$^{\cdot}$ the magneton number is zero. The magnetic susceptibilities of the oxides of manganese, and the oxides and sulphides of titanium and vanadium, are in general agreement with the above curve. The metals offer considerable difficulties, for the number of electrons which bind together the atoms is unknown. The work of Urbain and Janesch (cf. A., 1909, ii, 116) has demonstrated the existence of two groups within the rare earths, in each of which the magneton moment attains a maximum and then decreases. Qualitatively, the changes in magneton number will be analogous to that of the group studied above. These results do not appear to be in accord with the modification of the M levels assumed by Bohr, for this structure should lead to discontinuities in the curve of the magnetic moment.

The results of Stern and Gerlach (*Z. Physik*, 1922, **9**, 353) are not in opposition to the Weiss magneton. W. E. G.

Influence of the Pitch of Sound on the Measurement of the Relationship $k=c_p/c_v$ for Carbon Dioxide. BRUNO TORNAU (*Z. Physik*, 1923, **12**, 48—57).—The ratio of the specific heats for carbon dioxide was found to be $K_0=1\cdot3165\pm0\cdot00032$. Variation in the pitch of the sound produced no change in the value of K_0. W. E. G.

Atomic Heat of Simple Substances. EDM. VAN AUBEL (*Bull. Acad. roy. Belg.*, 1921, [v], **7**, 155—159).—The validity of certain conclusions drawn by Michaud (A., 1920, ii, 532) is discussed, making use of existing data for the specific heats, etc., of silicon, boron, rhombic sulphur, thallium, magnesium, and chromium. Michaud's conclusions are shown to be untenable. E. E. T.

Third Law of Thermodynamics. Evidence from the Specific Heats of Glycerol that the Entropy of a Glass exceeds that of a Crystal at the Absolute Zero. G. E. GIBSON and W. F. GIAUQUE (*J. Amer. Chem. Soc.*, 1923, **45**, 93—103).—An improved calorimetric apparatus is described for determinations at low temperatures. The specific heat of supercooled glycerol and the specific heat and heat of fusion of crystalline glycerol have been determined at temperatures down to 69·9°*K*. The specific heats of the glass and the crystals approach one another as the temperature is lowered and are almost identical below 140°*K*. The heat of fusion of glycerol at the melting point 291·00°*K* is 47·50 cal./gram or 4370 cal./mol. and the entropy of fusion is 15·02 cal./degree per mol. or 1·073 cal./degree per gram. The entropy of supercooled liquid glycerol exceeds that of crystalline glycerol by 5·6±0·1 cal./degree per mol. at 70°*K*, and it is concluded that this value will not be appreciably different at the absolute zero. J. F. S.

Mass Effect in the Entropy of Substances. E. D. EASTMAN (*J. Amer. Chem. Soc.*, 1923, **45**, 80—83).—The hypothesis that the expression for the mass effect in the entropy of all substances in which equipartition holds takes the same form as for monatomic gases is tested for all cases for which data are available. The results show that there is much evidence in support of the hypothesis, and none definitely contradicting it. Several approximate equations are given for the calculation of the entropy of diatomic gases and metals. J. F. S.

Physical and Chemical Transformations of Gibbs's Systems. TH. DE DONDER (*Bull. Acad. roy. Belg.*, 1920, [v], **6**, 315—328).—A thermodynamical treatment of systems consisting of phases as defined by Gibbs. The author adopts a point of view very slightly different from the usual one. E. E. T.

The Chemical Constants of the Halogens in the Monatomic and Diatomic Condition. F. A. HENGLEIN (*Z. Physik*, 1923, **12**, 245—252).—The chemical constants of chlorine, bromine, and

iodine have been calculated from the dissociation and vaporisation equilibria of these gases, and the values are in good agreement with those derived by Stern and Tetrode. For the monatomic gases, the following results were obtained for the chemical constants: chlorine +0·72, bromine +1·26, iodine +1·56, and for the diatomic gases, chlorine +0·02, bromine +1·50, and for iodine +2·55. Bromine and iodine have the highest chemical constant of any element. The heat capacity of solid bromine has been determined, and a Debye function given for the calculation of its specific heat. The chemical constants of the halogens in the diatomic condition increase slightly as the temperature rises. W. E. G.

Relation between the Absolute Melting, Boiling, and Critical Temperatures of Substances. EDM. VAN AUBEL (*Bull. Acad. roy. Belg.*, 1921, [v], 7, 469—472).—The value of *r*, a constant (according to Prud'homme, A., 1920, ii, 83, 84, 376; see also A., 1921, ii, 622) deduced from the absolute melting and boiling points and critical temperatures of various substances, has been calculated for a number of compounds, using existing data, and the following values of *r* have been obtained: Mercury 0·512, mercuric chloride 1·01, mercuric bromide 1·03, mercuric iodide 1·03, antimony trichloride 1·04, antimony tribromide 1·01, aluminium bromide 1·16, and aluminium iodide 1·10. All these substances, therefore, with the exception of mercury, give a normal value (*i.e.*, about unity) for *r*. E. E. T.

Method for the Determination of the Melting Point of Difficultly Fusible Metals. MARCELLO PIRANI and HANS ALTERTHUM (*Z. Elektrochem.*, 1923, 29, 5—8).—The melting point of metals with high melting point may be determined by using a hole (6 mm. deep and 1 mm. diam.) bored at an angle to the axis of a 7 mm. square rod of the metal, as a black body for temperature determination. That the metal had melted was indicated by drops of it falling from the hole. The heating was effected by passing a 50-period alternating current, which could be varied by steps of 10 amp. to 1500 amp., through the bar. Using this method, the melting point of tungsten and molybdenum has been determined and the values $3660° \pm 60°$ and $2840° \pm 40°$, respectively, have been obtained. These values are in agreement with other recent determinations. J. F. S.

Separation of Liquid Mixtures by Combined Distillation and Atmolysis. Preparation of Practically Pure Ethyl Alcohol and Nitric Acid. ÉDOUARD URBAIN and RÉMY URBAIN (*Compt. rend.*, 1923, 176, 166—168).—The apparatus consists of a distillation flask surmounted by a porous porcelain tube, which is jacketed with a glass tube in which the pressure can be reduced. The porous tube is fitted with a condenser on top, and is so arranged that the condensed vapours can be returned to the distillation flask or run into another vessel. With this apparatus, it is possible to obtain 99·8% alcohol by direct distillation. The water vapour passes through the wall of the porous tube, and the condensed

alcohol is returned to the distillation flask. In a similar manner, it is possible by means of this apparatus to prepare 99·6% nitric acid.
W. G.

The Heat of Oxidation of the Alkaline-earth Metals. A. Guntz and Benoit (*Compt. rend.*, 1923, **176**, 219—220).—The authors have made measurements of the heats of solution of calcium, strontium, and barium, respectively, in dilute hydrochloric acid, and from the results and the known heats of solution of their oxides in this acid have calculated the heats of oxidation of these metals to be 152·7, 141·8, and 134·04 cal., respectively. W. G.

Berthelot's Normal Acids and the Theory of Ions. F. Bourion (*Compt. rend.*, 1923, **176**, 95—98).—A theoretical discussion in which it is shown that in order to observe, in the progressive neutralisation of an acid by a base, differences between the values found and those calculated by proportionality by the current thermochemical methods, the affinity constant of the acid must not be greater than 10^{-10} with the usual order of magnitude of the heats of ionisation. W. G.

The Phenomenon of Molecular Association. Ettore Cardoso and Gabriele Battista (*Anal. Fis. Quim.*, 1922, **20**, 420—432).—From a combination of van der Waals's equation and the rule of Cailletet and Mathias, the densities of a liquid and its vapour, respectively, d_1 and d_3, are connected with the critical constants by the relation $d_1d_3/d_c^2=K(pT_c/p_cT)$, or more generally $d_1d_3/d_c^2=f(pT_c/p_cT)$. Deviations of this function from a linear relationship are attributable to molecular association and are the more pronounced the greater is the difference between the degree of association of the coexisting phases. The liquid phase is invariably more complex than the coexistent vapour phase.
G. W. R.

Cohesion Pressure, Surface Activity, and the Tendency to the Formation of Submicrons. I. Traube (*Kolloid Z.*, 1923, **32**, 22—24; cf. A., 1912, ii, 858; 1915, i, 105).—It has been shown previously that salts of alkaloids are molecular dispersed in aqueous solution (*loc. cit.*) and because of their ionic charge have a large cohesion pressure; they are therefore unable to form submicrons and have no surface activity. In every respect the reverse is the case for free, non-ionised alkaloids. It is now shown that the salts of fatty acids are similar to the salts of alkaloids in the above respects. With the exception of formic acid, the free fatty acids have a small cohesion pressure, and have a surface activity and from butyric acid upwards form submicrons. Here, as in the case of the alkaloids, the cohesion pressure decreases with increasing molecular weight, whilst the surface activity and the ability to form submicrons increases. The lower fatty acids, including propionic acid, do not form submicrons, whilst butyric acid forms many submicrons, and the higher fatty acids, such as nonoic, decoic, and undecoic acids, exist in both a surface active and an inactive form. Substances such as amyl alcohol, octyl alcohol, phenol, cresol,

aniline, and xylidine have a considerable cohesion pressure, and their concentrated solutions contain submicrons and molecular dispersed particles, whilst hydrocarbons and alkyl halides have small cohesion pressures, and in aqueous solutions exist mainly as submicrons. From the above facts, the author claims general validity for the rule previously put forward. The smaller the cohesion pressure, the greater is the surface activity and tendency to form submicrons.

J. F. S.

Films. Spreading of Liquids and the Spreading Coefficient. WILLIAM D. HARKINS and AARON FELDMAN (*J. Amer. Chem. Soc.*, 1922, **44**, 2665—2685).—It is found that the spreading of films is, in general, related to what is defined thermodynamically as the spreading coefficient. Liquids for which the value of this coefficient, S, is positive will spread, whilst those for which it is negative will not spread. Actually, the value of the coefficient refers to the system, spreading liquid-substance on which the spreading occurs, and may be quite different when A spreads on B, from what it is when B spreads on A. For example, most organic liquids have positive coefficients with reference to spreading on water, and therefore will spread into a film; but water has a negative coefficient with reference to most organic liquids and will not spread over them. The value of the coefficient, S, is defined by the equation $S=W_A-W_c$, in which W_A is the work of adhesion for the interface of the two liquids, and W_c the work of cohesion of the liquid which is applied to the surface of the other liquid or solid on which the spreading might occur. Thus a liquid will not spread if its work of cohesion, which indicates its attraction for itself, is greater than the work of adhesion, which indicates its attraction for the substance on which the spreading will not occur. The values of W_A and W_c are given by the equations: $W_A=\gamma_a+\gamma_b-\gamma_{ab}$; $W_c=2\gamma_b$, so that the value of the spreading coefficient may be entirely defined in experimental terms by the equation $S=\gamma_a-(\gamma_b+\gamma_{ab})$, where a indicates the liquid which is spreading on the liquid or solid represented by b. A large number of experiments have been made on the spreading of organic liquids on the surface of water, on the spreading of water on the surface of organic liquids, and on the spreading of water and organic liquids on the surface of mercury. The results show the importance of the spreading coefficient as a criterion of spreading. Unimolecular films are produced on water only when the spreading coefficient has a relatively high value. Since these high values seem to occur only when the spreading substance contains a polar group in its molecules, it is concluded that the presence of such groups is essential for spreading on water to a unimolecular film, but not at all essential for the production of a film which is thicker than this. Contrary to the generally held opinion, benzene is found to spread on a clean water surface. The non-spreading of organic liquids on water is brought about by the presence in the organic molecule of chlorine, bromine, iodine, doubly-linked sulphur, phenyl, and the group $=CS$. Liquids which do not spread on water are insoluble in it, but insoluble

liquids may spread on water. The addition of camphor to water appears to reduce the value of the spreading coefficient; so that many liquids which have small positive coefficients on water will not spread on water containing camphor, but those which have coefficients sufficiently high are found to spread. The values of the spreading coefficients of water and organic liquids on mercury are, in every case investigated, found to be positive. Water and twenty-two of the other liquids were tested with reference to their spreading on pure mercury, and in agreement with their positive coefficients were found to spread. The coefficients for the spreading of mercury on water and organic liquids are all negative. This corresponds with the fact that mercury will not spread on their surface. Since the free surface energy of almost all inorganic solids is high, their work of cohesion is high, and the work of adhesion is also high with reference to practically all liquid substances. Since the work of cohesion in water and organic liquids is in general low, the values of the coefficients of spreading of these liquids on such solids should be positive and in general the value should be high. Thus the spreading of these liquids should occur on such solids when the surfaces are pure. The frequently occurring phenomenon of non-spreading is thus indicated to be due to the presence of an already existent film on the solid substance. The removal of such films may be brought about by vaporisation, or by the more common process of substituting one film for another. This is the ordinary function of soap, soap solutions, and other cleansing agents. It is difficult for petroleum to penetrate sands which have been wetted by water, and for water to penetrate sands which have been wetted by petroleum, although either substitution may be effected in time. Many oil wells cease to produce petroleum because the sand becomes wet with water. Lubrication and many other phenomena depend on the wetting of solids by films. J. F. S.

Measurement of Adsorption Processes by Means of an Interferometer. OTTOMAR WOLFF (*Kolloid Z.*, 1923, **32**, 17—19).—Experiments are described to show that for industrial purposes an interferometer may be used to ascertain the amount of colloid adsorbed from solutions by any given adsorbent. J. F. S.

General Theory of the Adsorption of Solutions. WOLFGANG OSTWALD and RAMON DE IZAGUIRRE (*Kolloid Z.*, 1923, **32**, 57—64).—In answer to the criticisms of Gustaver (this vol., ii, 57), the authors admit that in their recent paper they have interchanged the values u and u_0 as used by Williams (*Medd. Nobel-Inst.*, 1919, **2**, No. 27, 1) owing to want of clearness in that paper. The authors deny that the equation which is put forward in their paper is the same as that due to Williams. The equation put forward by Williams is special and relates to a single case only whilst that due to the authors applies to three cases. In the best investigated case, the adsorption of acetic acid solutions by charcoal, the deduction made by Williams that $u_0=-\infty$ when $c=1$ does not hold. The new equation furnishes more and other results than that of Williams. The necessity of differentiating between relative and absolute

thicknesses of layers in the investigation of adsorption layers is emphasised. In the adsorption of colloid particles the adsorption layer cannot be unimolecular in thickness; it must be at least unimicellar. The adsorption layer may have very different thicknesses, depending on the size of the absorbed particles and on the amount of water which is adsorbed at the same time. The assumption of Gustaver that the adsorption layer has a maximum thickness of one molecule is further refuted by the ultramicroscopic observations of Traube and Klein (A., 1921, ii, 683) on adsorption layers of surface active emulsoids, which vary up to 0·01 mm. thick.

J. F. S.

The Sorption of Iodine by Carbons Prepared from Carbohydrates. JAMES BRIERLEY FIRTH (T., 1923, **123**, 323—327).

The Absorption of Moisture by Coal (and other Fuels). I. A Relation between Degree of Humidity in the Air and Moisture Content of Coal. BURROWS MOORE and FRANK STURDY SINNATT (T., 1923, **123**, 275—279).

Adsorption of Toluene Vapour on Plane Glass Surfaces. EMMETT K. CARVER (*J. Amer. Chem. Soc.*, 1923, **45**, 63—67).—Isotherms for the adsorption of toluene vapour on plane glass surfaces at 0° have been obtained. The glass used was, after thorough cleaning, kept at 200° in a vacuum for twelve hours and any gas set free removed by a mercury vapour pump. Pressure measurements were made with the author's modified Shrader and Ryder optical lever manometer (this vol., ii, 148). The results are generally in agreement with Langmuir's adsorption formula (A., 1918, ii, 430), and indicate that the adsorbed layer is not more than one molecule thick. J. F. S.

Fixing of Organic Dyes by Inorganic Substrates. H. RHEINBOLDT and E. WEDEKIND (*Koll. Chem. Beihefte*, 1923, **17**, 115—188).—The literature dealing with the fixing of organic dyes by insoluble inorganic substances has been collected and discussed. It is shown that acidic and basic dyes exhibit a different behaviour toward similar substrates. In particular, substrates of acidic character are only fast dyed by basic dyes, whilst acidic dyes only fast dye basic substrates. The results of various authors which appear to be at variance with the above rule are in reality not so, since they do not refer exactly to the same thing. A large number of experiments with many dyes and inorganic gels have been carried out and give results entirely in agreement with the above rule. This rule is not only true for acidic and basic oxides, of which the following were examined: silica and tin, titanium, zirconium, thorium, and cerium dioxides; aluminium, chromium, and iron sesquioxides; and glucinum, zinc, magnesium, and lead monoxides; but also for sulphides (arsenic, antimony, and cadmium), and silver chloride. In no case was a dye from both classes fixed, with the single exception of amorphous carbon. The electro-endosmotic migration of the dyes and inorganic substrates was investigated, and it is found that fast dyeing only takes place between substrate and dye when

they are oppositely charged. The authors are of the opinion that the unsaturated valency forces of the crystal lattice of the absorbent are responsible for the fixing of the dye. Since these valencies are identical with the normal chemical valency, the behaviour of the substrate is explained. And since the valencies are of an electrostatic character, the parallelism of the electro-endosmosis and the adsorption is understandable. The fixing therefore consists in the binding of the dye to the substrate to form a unimolecular layer of a molecular additive compound. This process the authors term *adsorption by electro-affinity*. It is held that the adsorption by electro-affinity is not restricted to substances which have ordered crystal lattices, and the charge of sols, gels, and other colloidal material is attributed to the action of the same surface valencies.

J. F. S.

Exact Process for the Determination of the Coefficient of Diffusion in any Solvent. ERNST COHEN and H. R. BRUINS (*Z. physikal. Chem.*, 1923, **103**, 349—403).—The authors have summarised and criticised the method available for the determination of the coefficient of diffusion. A process for the exact determination of the diffusion coefficient has been devised. The apparatus consists of six thick glass plates of the same diameter, which fit exactly on a firm central axis. The four middle plates are firmly fixed and three holes bored through them so that in each plate there are three holes relatively in the same position. These plates are placed between the other two, which constitute a base and a cover plate. The hole in the lowest bored plate is filled with the liquid of which the diffusion is to be measured, by means of a small hole which can be brought above it by rotating the necessary plates. The other three plates with holes are brought into such a position that the holes in them are above one another, but not above the hole in the lowest plate, and filled with the solvent. The arrangement now is that of two tubes filled with liquids, which by rotation of the bottom bored plate may be brought into contact. When the whole apparatus has reached the required temperature, the liquids are brought into contact and the diffusion commences. After a sufficiently long period, the plates are twisted so as to cut the column of liquid into four isolated parts and the composition of each is estimated by the Rayleigh Löwe interferometer. It is claimed for the apparatus that it may be used for all types of liquids, of which only small quantities are necessary. It may be used at any temperature over a wide range, and there is no error due to vibration or shaking when the liquids are brought into contact. By the use of an air thermostat, the temperature is known, and may be kept constant to 0·03°. The error of the method is not greater than 0·3%, and individual measurements are reproducible to 0·1—0·3%. J. F. S.

Validity of the Stokes-Einstein Law for Diffusing Molecules. ERNST COHEN and H. R. BRUINS (*Z. physikal. Chem.*, 1923, **103**, 404—450).—The validity of the Stokes-Einstein equation for the diffusion in solutions at various temperatures has been investigated by means of the diffusion apparatus previously

described (preceding abstract). The pair of liquids tetrabromoethane and tetrachloroethane has been used and the diffusion velocity measured at temperatures from 0° to 50°. The viscosity of tetrachloroethane has been determined over the same temperature range with a maximum error of 0·05%. Divergences from the Stokes-Einstein law have been observed which are at least three times as great as the experimental error. The divergences are in the sense that the temperature coefficient of the velocity of diffusion is smaller than would be expected. The following values of the relative viscosity of tetrachloroethane are recorded: 0°, 1·6219, 10·0°, 1·3113, 15°, 1·1924, 25°, 1·0000, 35°, 0·8541 and 50°, 0·6917. The absolute fluidity of tetrachloroethane is given by the formula $\phi/T=0\cdot13796\ (1+0\cdot0191710\theta+0\cdot000009256\theta^2)$. J. F. S.

The Capabilities of the Rapid Dialyser. A. GUTBIER, J. HUBER, and W. SCHIEBER (*Chem. Ztg.*, 1923, **47**, 109—110).—Further investigation of the rapid dialyser described previously (A., 1922, ii, 551). The effect of using tap water instead of distilled water for the outer liquid was studied, and it was found that 80—90% of the electrolytes can advantageously be removed from colloidal solutions by dialysing against tap water, after which point distilled water must be used. Experiments indicated that dialysis was more efficient the greater the speed of rotation of the membrane and stirrer; 100 revolutions per minute was satisfactory, with slightly greater efficiency at 150 per minute. Generally, a flow of 5 litres of water per hour in the outer vessel is sufficient. The use of more than 10 litres per hour produced no corresponding increase in the rate of dialysis. G. F. M.

The Law of Solution. PAUL MONDAIN-MONVAL (*Compt. rend.*, 1923, **176**, 301—304).—Measurements made with a very soluble salt, sodium nitrate, show that it obeys very exactly the equation established by Le Chatelier for the solubility of salts in water (A., 1885, 340; 1894, ii, 272). W. G.

Solubility and Chemical Constitution. H. J. PRINS (*Rec. trav. chim.*, 1923, **42**, 25—28).—It has been concluded by Harkins (A., 1921, ii, 242) and by Langmuir (A., 1917, ii, 19) that adsorption and solubility are closely related. Both authors attribute orientation phenomena exhibited by organic substances with water to the tendency of the polar group to dissolve in water. It is pointed out that the arbitrary circumstance that these researches were carried out with water and an organic substance containing a group more or less similar to water may lead to erroneous conclusions. With organic acids and water, solubility and adsorption are both caused by the same group, but this is not generally the case. A number of examples are given showing that solubility in hydrocarbons such as light petroleum depends, not on polar groups, but on saturated hydrocarbon groups. Solubility depends in general on similarity in kind and number of atoms present in the molecules of the substances in question. Adsorption represents a case of hetero-complex formation, whilst in solution the complexes have the character of homo-compounds. E. H. R.

Contraction on Solution of Various Substances in Water. JITENDRA NATH RAKSHIT (*Reprint Indian Assoc. Cultivation Sci.*, 1917, 3, pp. 1—21).—Making use of data from Landolt and Börnstein's tables, the author has calculated the contraction which takes place when 100 g. of various substances are dissolved in various quantities of water. The values have been calculated for sulphuric acid, nitric acid, formic acid, stannic chloride, acetic acid, methyl, ethyl, propyl, *iso*butyl, and *iso*amyl alcohols, glycerol, acetonitrile, acetone, nicotine, ammonia, hydrogen chloride, sodium and potassium hydroxides, sodium chloride, tartaric acid, chloral hydrate, phenol, sucrose, lævulose, dextrose, maltose, and invert-sugar. In some cases, the contraction increases with increasing dilution, whilst in others the contraction increases, passes through a maximum, and then decreases with increasing dilution. J. F. S.

Effect of Scratching the Wall of a Vessel with a Glass Rod. L. DEDE (*Z. Elektrochem.*, 1922, 28, 543); ROBERT FRICKE (*ibid.*, 1923, 29, 44—46).—A continuation of the controversy on the cause of crystallisation when the walls of a tube containing a solution are rubbed with a glass rod (cf. A., 1922, ii, 692, 744). J. F. S.

Viscosimetric Researches on Lyophilic Sols. H. G. BUNGENBERG DE JONG (*Rec. trav. chim.*, 1923, 42, 1—24).—The greater proportion of viscosity measurements recorded in the literature cannot claim an accuracy of more than a few per cent. The conditions necessary to attain an accuracy of 0·1 to 0·2% are discussed, and in particular the two most important sources of error, the systematic error of the viscosimeter and the method of setting the instrument. For a given capillary, there is a maximum average rate of flow for a given liquid so that the deviation from Poiseuille's law shall not be greater than 0·1%. A formula for calculating this rate was given by Grüneisen (*Wiss. Abh. Phys. Tech. Reichsanstalt*, 1905, 4, 151). By means of this formula, the systematic error of the viscosimeter and the necessary length and fineness of capillary can be calculated. The error of setting can be minimised by fixing the instrument so that the line joining the centres of the upper and lower reservoirs in the Ostwald viscosimeter is vertical, instead of one of the limbs. Measurements of viscosity recorded in the literature are subjected to a general criticism and in particular the work of Hatschek on the viscosity of gelatin sols (A., 1911, ii, 98; 1913, ii, 835), and that of Rothlin (A., 1920, ii, 18), is discussed. Hatschek observed with a number of lyophilic sols that the viscosity depends on the rate of flow or shear, and he supposes that this phenomenon supports the theory of a dodecahedral structure of concentrated lyophilic sols. Rothlin divides lyophilic sols into two groups, one of which follows Poiseuille's law, whilst the other does not. These deviations are to be ascribed to the formation of larger aggregates in the sol through gelation; these aggregates, according to the conditions of flow, can be broken down to different extents, and so give rise to the observed irregularities. This explains the fact, in the case of both Hatschek's and Rothlin's abnormal sols, that the

viscosity increased with time, due to progressive gelation. At higher pressures, such systems would approximate more and more closely to Poiseuille's law, as Rothlin found. It is concluded that, for viscosimetric measurements to have any value, the system under *examination must not only follow Poiseuille's law, but the disperse phase must retain its stability. Experiments with agar sols show that at 50°, that is, above the gelation temperature, agar sols follow* Poiseuille's law within 0·2%, although at 27° deviations of more than 100% are shown. Moreover, above the gelation temperature all hysteresis phenomena are absent, and mechanical treatment has no influence on the viscosity. The only alteration in viscosity with time shown by these sols is a slight decrease due to hydrolysis of the disperse phase. When such an agar sol is diluted with electrolytes, a final equilibrium is reached immediately.

It is suggested that the term sol should exclude all liquid systems (1) which show deviations from Poiseuille's law; (2) where the viscosity is influenced by mechanical treatment, (3) where gelation, coagulation, and ageing phenomena generally are present.

E. H. R.

Topo-chemical Reactions. Crystal Formation in Colloidal Metals. V. KOHLSCHÜTTER and K. STECK (*Z. Elektrochem.*, 1922, **28**, 554—568).—The frequent formation of silver crystals in solutions of colloidal silver has been explained partly on thermodynamic grounds as the result of solubility differences between silver particles of different sizes and partly as a result of the formation of crystal aggregates of the ultramicroscopic crystalline particles due to action of a molecular field. Both views are open to criticism; on the one hand, on account of the excessively small solubility of metallic silver, and, on the other, because of the constitution of the surface of colloidal particles. The author is of the opinion that chemical reactions are responsible for the crystallisation. It is shown that in eighteen months definite silver crystals form in Lea's sol, but in pure sols, prepared by the reduction of silver oxide with hydrogen, no silver crystals were visible until the sol had been kept for twelve years; the same applies to gels which are free from electrolytes and protective colloids and are preserved under water. Well-formed polyhedra are produced by the action of ferric-ions or silver-ions on coagulated gels and other forms of colloidal silver. Also the reduction of a silver-ion solution with ferrous-ions, within a definite range of concentration, produces a transient colloidally-dispersed metal which speedily forms crystals. The localisation of the reaction, by adding a solid ferrous salt to a solution of silver-ions or by adding a solid silver salt to a solution of ferrous-ions, accelerates the crystal formation. In keeping with the experimental results, the formation of crystals from colloidal solutions is to be regarded as due to a maturing process in consequence of the silver of the micellæ entering into the reversible reactions $Ag+Fe^{\cdot\cdot\cdot} \rightleftarrows Ag^{\cdot} + Fe^{\cdot\cdot}$ and $Ag+Ag^{\cdot} \rightleftarrows Ag_2^{\cdot}$, whereby the pressing together of the reaction products in and on the colloidal particles is probably determinative of the commencement of the reaction and also of the specific form-

ation of the crystalline silver. Observations on various oxides and sulphides lead to the view that, in the formation of crystals in colloidal systems, electromotive actions play a part. These are due to the formation of concentration cells in the colloidal systems.

J. F. S.

The Constitution of Colloidal Gels. J. DUCLAUX (*Bull. Soc. chim.*, 1923, [iv], **33**, 36—43).—A theory of the constitution of reversible gels is developed in which it is suggested that they are composed of three elements: the fluid which may be water or some other solvent, an insoluble solid forming with the fluid an irreversible gel, or sponge-like structure of ultra-microscopic cells, and a soluble solid dissolved in the solvent of the gel. The molecules or micellæ of this substance, which may be either crystalloid or colloid, are too large to be able to escape from the cellules of the sponge, but they are small enough for their solution to have a certain osmotic pressure in relation to the pure solvent. This solution is the "plasm" of the gel, and its swelling and expansion in a solvent are due to the osmotic pressure of the plasm. The limit of expansion is reached when equilibrium is attained between this osmotic pressure and the cohesion of the cellular structure of the gel. If the osmotic forces are strong enough, continued inflation of the cellules may result in the dissolution of the gel, and the separation of the soluble and insoluble constituents. The mechanical properties of the gel will evidently depend on the relative proportion of the two solid constituents, in gum arabic, or nitro-cellulose solutions prepared in the warm; the insoluble constituent is almost absent, and the tendency to gel formation is a minimum, but in gum-tragacanth, or cellulose-nitrate solutions prepared in the cold, the insoluble constituent dominates and manifests itself by gel formation or high viscosity. G. F. M.

The Influence of a Dissolved Crystalloid on the Rigidity of Gels. F. MICHAUD (*Compt. rend.*, 1922, **175**, 1196—1198).—By means of a method recently described (*ibid.*, 1922, **174**, 1282), the author has measured the rigidity of gels the moduli of which were less than any previously measured. The dissolved substances were added in solution to the liquid gel, the whole being allowed to set. The rigidity of gelose or gelatin gels is considerably decreased by the presence of acids or bases. In the case of gelatin, a strong acid exerts a more marked effect than a strong base, whilst the converse is the case if the gel is dilute. The curves obtained show that the action of the acid is a linear function of the concentration of the gel; that of the base is parabolic, so that addition to a gel of increasing quantities of base or acid eventually causes the base to exhibit a greater influence than the acid for equimolecular quantities. The disposition of the curves obtained for gelose is in the inverse sense. The author suggests that these results are consistent with the amphoteric properties of gelatin, and that, by analogy, gelose should be regarded as amphoteric, its basic being stronger than its acid function. The action of salts on the gel depends primarily on the amount hydrolysed: for those which

are not hydrolysed, the molecular lowering of rigidity is about one-tenth that of an acid or base. The action of organic substances is variable; sugars and glycerol have practically no effect, urea, urethane, and acetamide act similarly to mineral salts, whilst resorcinol, quinol, and, above all, tannin bring about a very much greater decrease than an acid or base. H. J. E.

Colloid Chemistry of Urate Jellies. E. KEESER and H. ZOCHER (*Koll. Chem. Beihefte*, 1923, **17**, 189—217).—An investigation of urate jellies, particularly those of lithium and sodium. It is shown that the jelly-forming urates belong to the class of electrolyte colloids and have properties which are parallel with those of soaps and similar substances. Microscopic examination of lithium urate jellies shows the presence of long, optically anisotropic, negative doubly refracting jelly particles and also of radial structures which extend into the rest of the jelly mass. The addition of methylene-blue to the long jelly particles produces a dichroic coloration, and the structure becomes fibrous. The dispersion of the double refraction is abnormal. The long structure of the particles cannot be confirmed by ultramicroscopic examination because of their size. Solutions of urates cannot be obtained in a viscous state like the anisotropic sols of vanadium pentoxide and benzopurpurin, neither do the urate solutions show streaming double refraction nor magnetic double refraction. Before lithium urate solutions pass into jellies, they become turbid, and after the jelly has formed, the turbidity, for the most part, disappears. It is suggested that the turbidity is due to droplets formed by an unmixing of the solution. Mechanically effected changes in the jellies are irreversible, that is, after displacement the jelly does not resume its original form when the displacing force is removed. The residue obtained by subjecting the jellies to pressure shows but slight swelling power. The rigidity of the jellies increases with increasing concentration of the solution of lithium urate from which they are formed. The rigidity of jellies of constant composition increases with increasing addition of a lithium salt, and the transformation into the crystalline condition takes place more slowly the more rigid the jelly. In all cases, crystallisation commences at a number of isolated but equally distributed points throughout the jelly mass. The addition of non-electrolytes such as carbamide, sugar, glycerol, or alcohols reduces the rigidity of the gels increasingly with increasing concentration, and retards the crystallisation generally. Carbamide is exceptional, inasmuch as it accelerates the crystallisation. Protective colloids are without effect on the jellies. Examination of the jellies by X-rays shows that particles of sufficient size to produce Röntgen interference figures are absent, whereas a similar examination of crystalline lithium urate gives very broad interference bands, which shows that the true size of the particles is considerably less than that of the needles visible in the microscope. Lithium urate is a negatively charged colloid. The residues obtained by drying the jellies are colloidal in character and have the power of adsorbing

gases. Thus 1 g. of lithium urate will adsorb 0·5 c.c. of nitrogen at atmospheric pressure. J. F. S.

Interfacial Tension between Gelatin Solutions and Toluene. S. E. SHEPPARD and G. S. SWEET (*J. Amer. Chem. Soc.*, 1922, **44**, 2797—2805).—The general relationship of the orientation of specific atom groups in the molecule to the emulsoid colloid state is discussed. A number of experiments on the separation of gelatin at a benzene-water interface have been carried out; these consisted in shaking 1·0%, 0·1%, and 0·01% aqueous solutions of gelatin with an equal volume of benzene at 30°, 40°, and 50° and measuring the volumes of the resulting benzene, water, and foam phases. The foam or interfacial layer consists of benzene dispersed in and protected by hydrated and aërated gelatin, and is partly stabilised. In further experiments, air was excluded and toluene substituted for benzene, and here it was found possible to shake the liquid without much separation of the gelatin in the toluene, although a considerable amount of toluene was emulsified in the gelatin solution. The stability of the gelatin foam at various hydrogen-ion concentrations was found to increase from both sides of the isoelectric point and to be most stable at this point. The interfacial tension of gelatin solutions of varying hydrogen-ion concentrations has been determined at 30°, 35°, and 40° by measuring the drop number of the solution. The drop number-hydrogen-ion concentration curves all lie above the corresponding curves for water, and all the gelatin solution curves show a characteristic break near the isoelectric point, the maximum reduction of interfacial tension being at $p_H=4·8$. J. F. S.

Classification of Disperse Systems in Connexion with the Mechanism of True and Colloidal Solution and Precipitation. P. P. VON WEIMARN (*Koll. Chem. Beihefte*, 1923, **32**, 72—114).—A survey of dispersoid chemistry in which classifications of disperse systems according to the state of aggregation of the particles and according to the "external" degree of dispersion are put forward. The imperfect nature of the static classification is pointed out, and a large number of tables are given of the appearance of precipitates of sparingly soluble substances at various times after their formation. J. F. S.

Velocity of Flocculation of Selenium Sols. H. R. KRUYT and A. E. VAN ARKEL (*Kolloid Z.*, 1923, **32**, 29—36).—The velocity of flocculation of selenium sols of various concentrations by solutions of potassium chloride and barium chloride of various concentrations has been determined at a series of temperatures from 15° to 20°. It is shown that the region of rapid flocculation for potassium and barium chloride lies at very high concentrations of these electrolytes. This result has been confirmed by measurements of the boundary charge of the sols. The results show that Smoluchowski's theory is valid in the region where the velocity of flocculation is not far removed from that obtaining when the colloidal particles are totally discharged. The results deviate

strongly from this theory when smaller concentrations of electrolytes are used; the divergence consists in a continuously decreasing velocity of flocculation. The boundary charge of the sols has been determined in the presence of a solution of various concentrations of potassium chloride, barium chloride, potassium hydroxide, and hexamminecobaltic chloride. It is shown that the addition of hydrazine increases the boundary potential, and that after the addition of ten m.mols. of barium chloride the particles still possess a charge. The addition of potassium hydroxide increases the boundary potential, and it is therefore suggested that the like action with hydrazine is due to hydroxyl-ions. J. F. S.

Colloidal Phenomena in Paintings. CH. COFFIGNIER (*Bull. Soc. chim.*, 1923, [iv], **33**, 128—132).—The thickening or swelling of the paint in oil paintings is a colloidal phenomenon, and is attributable to the action of the resin acids in the varnish on the lead or other heavy metal compounds used in the paint, whereby a colloidal metallic complex is formed which behaves as a reversible gel. The phenomenon is particularly noticeable and rapid with colophony varnishes, but it also occurs with other materials possessing free acidity. Congo and kauri gums, for example, whilst not behaving in this way with white lead, show the reaction with litharge or zinc white, but it can be prevented in all cases by eliminating the free acidity of the resin or gum. For this purpose, neutralisation with calcium carbonate or hydroxide is not so satisfactory as esterification, as the "neutralised" material has still a certain acid value which is not reduced to zero even by calcium hydroxide. Esterification of the gum or colophony with glycerol furnishes a material from which a neutral varnish can be prepared, and the troublesome phenomena above referred to then no longer occur, even with litharge or zinc white. G. F. M.

General Nephelometry. M. U. C. Al. LEDNICKÝ (*Kolloid Z.*, 1923, **32**, 12—17).—A general discussion of the application of nephelometry to colloidal solutions. It is shown that in comparisons it is essential that the illumination should be uniform and symmetrical; the beam of light should be horizontal and parallel. The surfaces of the solutions should be the same height and the concentration such that Beer's law holds, and so low that the boundaries of the Tyndall cone are sharp. The light should be monochromatic, and in the case where the two solutions have not the same colour a filter must be used before the light reaches the eye. J. F. S.

Non-, Uni-, and Bi-variant Equilibria. XXII. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **25**, 341—353).—In continuation of previous work (A., 1922, ii, 430), the author has investigated mathematically the condition determining the equilibrium of n components in a system comprising $n+1$ phases, when the quantity of one of the components is infinitesimally small, and has examined more especially the effect of a small quantity of added substance on a non-variant equilibrium. Expressions are derived for the partition of the added substance

between the various phases and for the temperature and pressure changes respectively occurring on such addition. F, L, and G representing the respective phases, it is shown that when a substance x is added to a system in non-variant unary equilibrium, $E(x=0)=F+L+G$, an equilibrium arises which is represented on the P—T diagram by a curve commencing at the non-variant point of the equilibrium $E(x=0)$. When the added substance occurs in the liquid phase only, this curve corresponds with the curve $L=F+G$ of the system $E(x=0)$. If the added substance occurs both as liquid and vapour, then the equilibrium curve is situated in region F, and its direction is determined by the partition of x between the vapour and liquid phases. When the added substance occurs both in the liquid and solid phases, the curve is situated in the region G, and its initial direction is determined by its partition between mixed crystals and liquid. In the case when the added substance occurs in the three phases, the curve may be situated in any of the three regions L, F, or G. Its direction is then defined by the partition of the added substance between the three phases. J. S. G. T.

Determination of the Chemical Equilibria between Various Stages of Oxidation by Means of Electrometric Measurements. I. The Equilibrium between the Sulphates of Bi-, Ter-, and Quadri-valent Manganese in Sulphuric Acid Solution. G. GRUBE and K. HUBERICH (*Z. Elektrochem.*, 1923, **29**, 8—17).—Oxidation potential measurements of mixtures of the sulphates of manganese in sulphuric acid of various concentrations have been made for a large number of solutions at 12°. It is found that in a solution which contains 0·05 g. atom of manganese in a litre of $15N$-sulphuric acid when at 12° the ratio of the stages of oxidation is 1 : 1, the following oxidation potentials exist: $\epsilon^{\circ}_{Mn^{II}\rightarrow Mn^{III}}=1·511$ volts, $\epsilon^{\circ}_{Mn^{III}\rightarrow Mn^{IV}}=1·642$ volts, and $\epsilon^{\circ}_{Mn^{II}\rightarrow Mn^{IV}}=1·577$ volts. These potentials are slightly dependent on the total concentration of manganese, but strongly dependent on the concentration of the acid. Increasing concentration of acid displaces the values to less positive potentials. Using the measured potentials, the equilibrium constant of the reaction $Mn_2(SO_4)_3 \rightleftharpoons MnSO_4+Mn(SO_4)_2$ was calculated. This value also changes with the acidity and the total concentration of manganese, and has been determined for a total manganese concentration of 0·05 g. atom per litre in concentrations of sulphuric acid varying between $9·1N$ and $24·2N$. From the determinations, it is shown that a $0·05M$-solution of manganic sulphate in $9·1N$-sulphuric acid decomposes according to the above equation to the extent of 36%, but in $24·2N$-sulphuric acid to the extent of 6·7%, that is, the equilibrium is displaced toward the left of the equation with increasing concentration of acid. The existence of this equilibrium is the cause of the abnormal behaviour of manganic sulphate on hydrolysis. With this substance, hydrolysis produces manganous sulphate and a hydroxide of quadrivalent manganese. This is due to the fact that of the components of the equilibrium, quadri-

valent manganese sulphate, $Mn(SO_4)_2$, is most easily hydrolysed, whereby the equilibrium is disturbed and still more sulphate is produced, so that the reaction takes place completely from left to right. J. F. S.

Equilibrium Gelatin–Hydrochloric Acid. R. DE IZAGUIRRE (*Kolloid Z.*, 1923, **32**, 47—51).—It is shown that the view put forward by Lloyd and Mayes (A., 1922, i, 280) on the basis of measurements of the hydrogen-ion concentration in solutions of gelatin containing hydrochloric acid, that at concentrations below 0·04*N* the hydrochloric acid is attached to the amino-group and at higher concentrations to the nitrogen atom of the polypeptide group, cannot be substantiated from the measurements. So far as the accuracy of the measurements permits, it must be held that they point rather to a continuous curve for the hydrogen-ion combination curve. But from this it does not follow that a chemical combination has taken place between the hydrochloric acid and the gelatin, for a logarithmic equation similar to the adsorption equation leads to a similar curve. It is also shown that the change of the electric charge of an adsorbent during an adsorption process can lead to curves of the most divergent type. Since such changes do take place during the adsorption of ions, the point has to be settled whether the combination with ions is to be regarded as a chemical process or merely as an adsorptive process. J. F. S.

The Dissociation of Silver Sulphate. (MLLE) G. MARCHAL (*Compt. rend.*, 1923, **176**, 299—301).—The decomposition of silver sulphate under the influence of heat gives rise to an equilibrium reaction forming a bivariant system which becomes univariant if care is taken to have in the gaseous phase only the gases coming from the decomposition. The author has made a study of this equilibrium under these conditions. Above 660°, silver sulphate decomposes according to the equation

$$Ag_2SO_{4\,liq} \rightleftharpoons 2Ag_{sol}+SO_{2\,gas}+O_{2\,gas}$$

and there exists in the gaseous phase a small amount of sulphur trioxide to satisfy the equilibrium

$$2SO_{3\,gas} \rightleftharpoons 2SO_{2\,gas}+O_{2\,gas}$$

Using the equation $q=[4{\cdot}57(\log K_2-\log K_1)T_1T_2]/(T_2-T_1)$, the heat absorbed in the decomposition is calculated as 82·4 cal. between 820° and 1000°. Using Nernst's equation, the values obtained are 103·9 cal. at 820° and 103·2 cal. at 1000°. By means of the experimental results it is possible to calculate the state of equilibrium of the bivariant system for each temperature if it is arranged for the pressure of the oxygen at equilibrium to be equal to 1/5 atmos. pressure of the oxygen in the air. W. G.

Equilibrium of the Reaction between Metallic Silver, Cupric Chloride in Aqueous Solution, and Solid Cuprous and Silver Chlorides. GRAHAM EDGAR and LAWRENCE S. CANNON (*J. Amer. Chem. Soc.*, 1922, **44**, 2842—2849).—The reaction $CuCl+AgCl+H_2O=CuCl_2+H_2O+Ag$ has been investigated in the presence of hydrochloric acid of various concentrations

at 25° and 40°. The equilibrium constant has been obtained from both sides. The method is to shake the reagents together in coloured bottles and analyse the solution after equilibrium has been attained. The equilibrium constants have been calculated, making use of the principle of "ionic strength" and the values $1{\cdot}86\times10^{-6}$ for 25° and $1{\cdot}61\times10^{-6}$ for 40° obtained. From these values, the increase in the heat content of the system is calculated by means of the expression $\Delta H=RT^2d.\log_e K/dT$ and the value -1755 cal. obtained. The increase of free energy of the system is calculated for 25° and the value $\Delta F=7820$ cal. obtained. These values have been compared with the values obtained by Noyes and Ellis (A., 1918, ii, 27), Lewis and Lacey (A., 1914, ii, 521), and Noyes and Chow (A., 1918, ii, 214), and a moderate agreement has been found between the two sets of values. The present data afford a measure of support for the methods employed by Lewis and Randall (A., 1913, ii, 29) in calculating the activities of mixed electrolytes. J. F. S.

Liesegang Rings. I. Silver Chromate in Gelatin and Colloidal Gold in Silicic Acid Gel. EARL C. H. DAVIES (*J. Amer. Chem. Soc.*, 1922, **44**, 2698—2704).—The author has investigated the influence of gravity and light on the formation of silver chromate rings in gelatin and gold rings in silicic acid gel. A jelly composed of 0·14 g. of potassium dichromate, 4 g. of gelatin, and 120 g. of water was brought into contact with a solution of 8·5 g. of silver nitrate in 100 c.c. of water, the jelly being held in various positions so that diffusion could occur vertically downward and upward and also horizontally. It is found that diffusion is slowest when it operates against gravity, but the effect of gravity may be counterbalanced by hydrostatic pressure. The mechanism of the ring formation is as follows. The silver nitrate diffuses into the gelatin and gives what appears to be an opaque region which in reality consists of opaque bands; these preliminary bands are further apart as the distance from the surface increases. These preliminary bands are due to the unequal rate of diffusion of the nitric acid and potassium nitrate produced in the reaction. The groups of silver chromate–potassium nitrate crystals, which are seen microscopically to form, are gradually broken up as the potassium nitrate diffuses away and the silver chromate particles become larger because of the oncoming silver nitrate. Hence the small bands lose their identity and the large bands are formed. Colloidal gold in silicic acid gel produced no rings when kept at 0° in the dark for nine days, but only isolated gold crystals. On placing these tubes in a powerful beam of light for an hour a band 1·5 cm. thick was formed. The band did not commence as a thin line and grow, but the whole area developed a faint yellow colour at once, and this grew in intensity as the exposure proceeded. A further tube of colloidal gold in silicic acid gel was covered with black paper and at distances of 9 cm., 2 cm. bands were cut away. The tube was placed in a dark room and the light from an 80 watt lamp fell on it for nine days, when slightly green colloidal bands

developed at the openings. A similar tube showed no bands after keeping for six days in the dark, but on exposure for a few minutes to an arc light bands developed at the openings in the paper, but no bands appeared between the openings. The tube was kept for for a further seven days in the dark at 0°. The paper was then entirely removed and the tube exposed to an arc light for three hours, when a slight blue colour developed between the original bands. J. F. S.

Liesegang Rings. II. Rhythmic Bands of Dyes on Filter-paper and Cloth by Evaporation. Refractivity, Surface Tension, Conductivity, Viscosity, and Brownian Movement of Dye Solutions. EARL C. H. DAVIES (*J. Amer. Chem. Soc.*, 1922, **44**, 2705—2709; cf. preceding abstract).—Rhythmic bands of dyes have been produced on filter-paper, cotton cloth, and unglazed porcelain by regulated evaporation. Solutions of some sixty-two dyes were used in 0·04% and 0·005% concentrations with several varieties of filter-paper. A table is given in which the following physical properties of the 0·04% solutions are recorded: refractive index, surface tension, electrical conductivity, viscosity, and Brownian movement. The Tyndall cone and band formation are also investigated and the data recorded. It is shown that a uniform temperature and a gradual decrease in the rate of flow are the important factors in the formation of bands. It is probable that just before the band forms a film of oriented molecules is present. J. F. S.

Calculation of Velocity Constants. A. L. TH. MOESVELD (*Z. physikal. Chem.*, 1923, **103**, 481—486).—The author describes a method of calculating the velocity constant of a reaction which is more accurate and less arbitrary than the generally adopted method. The velocity equation for a reaction of the nth order can be written in the form $1/(A-x)^n=k't+1/A^n$, where x is the concentration at time t and A at $t=0$. The method consists in inserting the values of $A-x$ and t in the equation for each measurement and so obtaining a series of equations with two unknowns, k' and $1/A^n$. When these equations are solved by the method of least squares, the value of k' is obtained which corresponds most nearly with the whole of the experimental results. Further, from the divergence of the experimental value of $1/(A-x)^n$ and the value calculated from k', it is at once shown whether the equation chosen is the correct one for the case under examination. A simplified method of working out the rather complicated calculations is given. J. F. S.

The Speed of the Uniform Movement of Flame in Mixtures of the Paraffins with Air. WALTER MASON (T., 1923, **123**, 200—214).

The Roaring of the Bunsen Burner Flame. KARL GLASER (*Z. angew. Chem.*, 1923, **36**, 38).—The phenomenon of the roaring of the flame of the Bunsen burner is not a peculiarity of any particular gas, but can be caused with any gas by sufficiently

increasing the pressure above the normal, whereby a corresponding increase occurs in the velocity of flow, other things remaining equal. The conditions governing the phenomena may be expressed as follows, where v is the velocity of flow, c the velocity of the propagation of flame for the gas in question, v' a factor depending on the buoyancy of the gas, and c' on the preliminary heating to which the gas is subjected in the burner: when $v+v'<-(c+c')$ the flame strikes back; when $v+v'=-(c+c')$ the burner burns normally, and when $v+v'>-(c+c')$ the flame roars. G. F. M.

Piezo-chemical Studies. XVII. Influence of Pressure on the Velocity of Reaction in Homogeneous Liquid Systems. A. L. TH. MOESVELD (*Z. physikal. Chem.*, 1923, **103**, 486—504).—The pressure coefficient of the velocity of reaction of the change $5HBr+HBrO_3=3Br_2+2H_2O$ between the temperatures 1° and 39° has been determined. It is shown that for the temperature range examined it is independent of the temperature. The velocity of reaction at a pressure of 1500 atm. is 15·4% less than that at 1 atm. pressure. The pressure influence is therefore negative and very much smaller than that observed in cases of hydrolysis carried out under approximately similar conditions. From this it is to be concluded that pressure exerts a specific influence on the velocity of reaction, and this is not changed by changing the external conditions under which the reaction is taking place.

J. F. S.

Regularities in the Velocity of Vaporisation. W. HERZ (*Z. Elektrochem.*, 1922, **28**, 526—527).—It has been shown recently by Volmer and Estermann that the velocity of vaporisation, G, is given by the equation $G=1/\sqrt{2\pi R}\times p\sqrt{M/T}$, where p is a constant, M the molecular weight, and T the boiling point in absolute degrees (A., 1922, ii, 193). This indicates that $\sqrt{M/T}$ is proportional to G. The author has calculated the values of $\sqrt{M/T}$ for a large number of substances, and finds that the value increases steadily with the molecular weight in homologous series; it also increases with the replacement of hydrogen by chlorine. The removal of two hydrogen atoms and consequent formation of a double linking reduces the value, whilst the formation of a treble linking causes a still further and much larger decrease. Ethers generally have much larger values than the corresponding saturated hydrocarbons. J. F. S.

Solubility and Specific Rates of Hydrolysis of ββ′-Dichlorodiethyl Sulphide in Water. ROBERT E. WILSON, E. W. FULLER, and M. O. SCHUR (*J. Amer. Chem. Soc.*, 1922, **44**, 2867—2878).—The hydrolysis of ββ′-dichlorodiethyl sulphide in water has been investigated. It is shown that the hydrolysis in contact with water is a two-phase reaction which affects only the molecules dissolved in the aqueous phase. The rate of the first stage of the reaction determines that of the second stage. Once steady conditions are established, the concentration of the intermediate compound automatically increases or decreases, keeping the rate of the second stage just equal to that of the first stage. The

amount of intermediate compound present at any time is extremely small, and the time required to build up the equilibrium concentration is generally negligible. The simplest expression for the rate of hydrolysis at 25° in alkaline solutions, where there is no tendency toward reversal, is $dc/dt=2K_1(M)=0{\cdot}304(M)$, where dc/dt is the rate of hydrolysis in millimols. of hydrogen chloride produced per litre per minute and (M) is the concentration of gas in millimols. per litre. The second stage of the hydrolysis is substantially non-reversible except in very concentrated hydrochloric acid solutions. The first stage is, however, reversible to a considerable extent even in the presence of dilute acids. This reversibility of one stage serves to retard, but not to stop, the reaction, because the intermediate compound of the hydrolysis is being continually destroyed by the irreversible second stage. Indirect evidence indicates that the second stage of the reaction is catalysed in direct proportion to the hydrogen-ion concentration in acid solutions. Since the rate is also very rapid in alkaline solutions, it is very likely catalysed also by hydroxyl-ions. The mathematical expression for the rate of hydrolysis in acid solutions is $dc/dt=K_1(M)-k_1(I)(H^{\cdot})(Cl')+k_2'(I)(H^{\cdot})$. A simpler but less obviously rational form of this equation is $dc/dt=2k_1(M)/(1+k_3(Cl')=0{\cdot}304(M)/(1+6{\cdot}14(Cl')$. This equation has been found satisfactory for a wide range of acid concentrations. The solubility of ββ'-dichlorodiethyl sulphide in water at 25° is 0·0043 mol./litre, and on substituting this value in the equations above the rate of hydrolysis in saturated solutions is obtained.

J. F. S.

Velocity of Hydrolysis of Methoxymethyl Acetate. ANTON SKRABAL and MARIA BELAVIĆ (*Z. physikal. Chem.*, 1923, **103**, 451—460).—The velocity of hydrolysis of methoxymethyl acetate in 0·1M-solution by 0·1, 0·05, 0·02, and 0·01N-hydrochloric acid, 0·1N-sodium carbonate, and 0·1N-sodium metaborate has been determined at 25° and the values obtained have been compared with the values previously obtained (A., 1921, ii, 134) for the simple acetals, methylal, and methylene diacetate. The mixed acetal is hydrolysed much more rapidly in acid solution than the two simple acetals, whilst the velocity in alkaline solution lies between that of the two simple acetals. J. F. S.

Energetics of Sucrose Inversion. THOMAS MORAN and HENRY AUSTIN TAYLOR (*J. Amer. Chem. Soc.*, 1922, **44**, 2886—2892).—The effect of temperature on the potential difference of the normal hydrogen electrode is discussed, and it is shown from $E.M.F.$ measurements with acetic acid that it is approximately proportional to the absolute temperature. Measurements have been made on the very short ultra-red absorption of aqueous solutions of sucrose, dextrose, and lævulose in the region 0·75—1·0 μ. Sucrose and lævulose show a band at 0·875 μ which is not present with dextrose. The bearing of these results on the critical increment of sucrose dihydrate and on the mechanism of the inversion of sucrose has been discussed. J. F. S.

Process for Studying the Velocity of Formation of Precipitates. ROGER G. BOUSSU (*Compt. rend.*, 1923, **176**, 93—95).—A modified form of Jolibois's apparatus for studying the mixture of liquids (A., 1920, ii, 107) is used. The bottom limb of the Y-tube is cut off, and the two side limbs are so adjusted that their orifices are 1 cm. apart. The liquids necessary to form the precipitate are run at the same rate down the side tubes and mix almost immediately. The resulting mixture is allowed to flow into a large volume of water saturated with respect to the precipitate the formation of which it is desired to study. This volume of liquid is held at different distances below the point of mixing, and thus the time for the formation of the precipitate is varied. The diluted mixture is filtered at once and the precipitate collected and weighed. The errors do not exceed 5%. W. G.

Catalysts and Chemical Equilibrium. J. CLARENS (*Bull. Soc. chim.*, 1923, [iv], **33**, 43—48).—Polemical. A reply to Durand's criticism (A., 1922, ii, 701) of the author's original paper (A., 1922, ii, 436). G. F. M.

The Catalytic Action of Hydrogen-ions in the Hydrolysis of Esters. S. C. J. OLIVIER and G. BERGER (*Rec. trav. chim.*, 1922, **41**, [ii], 637—645).—An examination of the rate of hydrolysis, under various conditions, of benzyl chloride, α-chlorohydrin, ethyl nitrate, and methyl trichloroacetate showed that the presence of hydrogen-ions has practically no effect on the speed of the reaction in the case of the two first-named substances, a very small effect with ethyl nitrate, and a small but quite definite catalytic action with methyl trichloroacetate. The facts observed together with those described by Cavalier (A., 1899, ii, 13), Wegscheider (A., 1902, ii, 493), and Klemenc (A., 1918, i, 220), lead to the conclusion that hydrogen-ions have little or no effect on the hydrolysis of esters of strong acids. In a brief discussion of the mechanism of the reaction, the authors state that theories based on the supposed activation of the water by the acid (Rohland, A., 1901, ii, 152; Noyes and Sammet, A., 1902, ii, 498) are not satisfactory, as water should also be activated in the case of esters derived from strong acids. The theory of formation of oxonium salts put forward by Stieglitz (A., 1908, ii, 167) is preferred, because an increase in the negative character of the group R in R·CO·O·R′ decreases the basic character of the oxygen and consequently diminishes the tendency to form such salts (cf. Kendall and Booge, A., 1916, i, 707). It is uncertain whether the hydrolysis is effected by the ion $R'CO_2R'$-H, or by activation of the ester at the moment of conversion into oxonium salt. H. J. E.

Catalase Action of Peroxydase. E. ABEL (*Z. Elektrochem.*, 1922, **28**, 489—496).—It is shown that peroxydase catalyses the reaction between potassium iodide and hydrogen peroxide only in the presence of hydrogen-ions; in faintly alkaline solution, there is no acceleration of the velocity of reaction. The peroxydase

was obtained from horse-radish, and is seen in the above-mentioned reaction to exercise the action of a catalase (cf. A., 1920, ii, 35, 180). J. F. S.

The Fine Structure of Atomic Nuclei, and the Deviation from Coulomb's Law in the Interior of the Nucleus. I. The Atomic Nuclei of Lithium and *iso*Helium. MAXIMILIAN CAMILLO NEUBERGER (*Ann. Physik*, 1923, [iv], **68**, 574—582).—A theoretical paper in which it is shown that the deviations from Coulomb's law become smaller as the atomic number increases (cf. Smekal, *Sitzungsber. Akad. Wiss. Wien*, 1920, **130**, 149—157). In this paper the atoms of lithium (atomic weight=6) and *iso*helium are examined. The lithium atom is assumed to consist of two α_3-particles (*iso*helium) rotating in a ring around a β-particle. This arrangement is stable, and making allowance for the deviation from Coulomb's law, it is shown that the heat of formation of one gram-atom of $Li^6=4{\cdot}72\times10^7$ Cal. The heat of formation of *iso*helium from three hydrogen atoms is $Q=4{\cdot}72\times10^8$ Cal. The deviation from Coulomb's law is considerably greater for *iso*helium than for the Li^6 nucleus. It is shown that B^9 is unstable, which is in agreement with Aston's work on the isotopes of boron. The upper radius for the Li^6 nucleus is $2{\cdot}53\times10^{-13}$ cm., and for *iso*helium $1{\cdot}45\times10^{-13}$ cm. W. E. G.

The Stability of Atomic Nuclei, the Separation of Isotopes, and the Whole Number Rule. WILLIAM D. HARKINS (*J. Franklin Inst.*, 1922, **194**, 329—356, 521—535, 645—681, 783—814; **195**, 67—106; cf. A., 1922, ii, 702).—A summary of previous work on the stability and methods of separation of isotopes, and a review of the theory of Harkins and Wilson (A., 1915, ii, 543, 544) of the evolution of atomic species from hydrogen atoms and α-particles, and the experimental evidence in its favour. From the relative abundance of the different atomic species in meteorites and in the earth's crust, deductions are made as to the relative atomic stabilities and the part played by the ratio of the number of protons to electrons in the nucleus in determining the order of stability (cf. A., 1922, ii, 490). Five stability principles are enunciated, (1) no nucleus is stable unless the number of electrons it contains is equal to, or greater than, one-half the number of protons ($N/P>0{\cdot}5$), (2) as the nucleus becomes more positive with reference to its net content of protons, it is essential for stability that it shall become more negative with respect to its relative content of electrons, (3) the number of electrons in most nuclei is even, (4) atomic nuclei, and groups of protons and electrons in atomic nuclei, are in general more stable when they contain an even, rather than an odd, number of protons, and (5) elements of an even atomic number are much more abundant than those of odd atomic number. The determining factor for stability is the ratio N/P. The principles for the prediction of isotopes from the chemical or mean atomic weights are illustrated by means of the element lithium, for which isotopes with atomic weights 6 and 7 should exist. For the hypothetical atom with atomic

weight 5, $N/P=0.4$, and for that with atomic weight 8, $N/P=0.625$, which is higher than the ratio for any known atomic species. Hence it is concluded that these forms of lithium are incapable of existence. The principle that the most abundant isotopes of elements with even atomic weights will also possess even atomic weights has received support from the work of Dempster on the isotopes of zinc, and of Aston on the isotopes of tin. In general, the most abundant isotope of an element has a charge and a mass equal to a whole number times the charge and mass of an α-particle. The original theory of Rutherford, that the light atoms are built up mostly of particles of mass 3, was not justified. The mode of disintegration of the light atoms by the Rutherford method and the disintegration of the radioactive elements are discussed. Calculations are made of the energy of disintegration of the radioactive elements. In conjunction with Lunn, the loss of electromagnetic mass due to the approach of protons to electrons has been derived (cf. A., 1922, ii, 703). The possibility of distinguishing between isotopes by spectroscopic measurements is considered, and it is concluded that isotopes should differ chemically. A summary is given of the methods previously employed in the separation of the isotopes of neon, chlorine, and mercury, and of the efficiencies of the processes of distillation, diffusion, and liquid centrifuging. Evidence is submitted of the separation of cadmium and zinc, by a distillation method, to the extent of 0·04 to 0·05 of a unit of the atomic weight. W. E. G.

A Relation between the Atomic Numbers and the Atomic Weights of the Chemical Elements. F. Loewinson-Lessing (*Compt. rend.*, 1923, **176**, 307—309).—The sum of the atomic numbers of two adjacent elements starting from helium give the following relationships: for the first twenty elements the atomic weight is equal to + or −1 to the sum of the atomic numbers of the element and of that which immediately follows it. Starting from scandium this atomic difference between the atomic weight in round numbers and the sum of the atomic numbers increases and reaches a value of 51 at the finish, but in certain groups of elements its value remains almost constant. There is in the horizontal rows of the periodic system a certain regularity in its increase. This correlation allows the atomic weights of the five elements not yet discovered to be foretold and atomic weights of certain elements to be corrected.

W. G.

Radicles and the Periodic Classification of the Elements. A. Ríus y Miró (*Anal. Fís. Quím.*, 1922, **20**, 496—500).—The atomic number of a radicle may be obtained by subtracting from the sum of the atomic numbers of its constituent elements twice the number of valencies concerned in its formation. For example, in the case of ammonium the atomic number is $7+(4\times1)-(2\times4)=3$, equal to the atomic number of lithium. Atomic numbers for other radicles calculated in the same way enable them to be assigned to appropriate positions in the periodic classification. G. W. R.

The Ångström System of Units. T. M. LOWRY (*Rec. trav. chim.*, 1923, **42**, 29).—The proposal of Centnerszwer for the introduction of a unit of atomic mass (*ibid.*, 1922, **41**, 580) has been anticipated by Sir W. H. Bragg (*Proc. Phys. Soc.*, 1921, **34**, 35), who proposed that the Ångström unit of length, 10^{-8} cm., should be made the basis of a unit of area 10^{-16} cm.^{2}, of volume 10^{-24} cm.^{3}, and of mass 10^{-24} g. The mass of an atom in Ångström units is then 1·65 times its atomic weight. E. H. R.

Molecular Dimensions, Molecular Structure, and the Viscosity of the Halogens and their Hydrides. HARRY SCHMIDT (*Z. Physik*, 1923, **12**, 24—27).—An extension of the equations of Chapman (A., 1916, ii, 416). The mean molecular collision area of chlorine, bromine, and iodine have been derived by Rankine (A., 1921, ii, 192) from viscosity determinations, and from these values, on the assumption that the halogen molecule consists of two atoms in contact, the atomic radii have been calculated. From these figures and the radius of the hydrogen atom, given by the Bohr theory, the mean collision area of the hydrogen halides is derived, and compared with data based on viscosity measurements. The agreement is satisfactory. On the other hand, measurements of the viscosity of hydrogen give values for the mean collision area which are not in accord with the assumption that the hydrogen molecule consists of two hydrogen atoms in contact. W. E. G.

Magnetic Valency and the Radiation Hypothesis. F. T. PEIRCE (*Phil. Mag.*, 1923, [vi], **45**, 317—323).—An inquiry into a possible mechanism of chemical change which would assign an effective rôle to radiation of a definite frequency. A theory of the valency bond is put forward which is based on the work of Oxley (cf. A., 1921, ii, 82). The valency bond is due to the magnetic attraction between two ring or vortical electrons, and can only be destroyed by the influence of radiation of the right frequency. The effects of temperature radiation and external illumination are discussed and compared, and the conclusion is drawn that photocatalysis should be observable only where the rate of reaction is determined by a dissociation. W. E. G.

Transformations in Unsaturated Compounds. Negative Migration. A New Theory of the Conjugated System C:C·C:C. ALFRED GILLET (*Bull. Soc. chim. Belg.*, 1922, **31**, 365—375; cf. A., 1921, i, 490, 533, 761).—A theoretical discussion in which the author maintains that by generalising two or three types of transformation of which several cases are known, the properties of conjugated double bonds may be explained without assuming the existence of partial valencies. H. J. E.

The Metallurgical Applications of Physical Chemistry. CECIL HENRY DESCH (T., 1923, **123**, 280—294).—A lecture delivered before the Chemical Society on December 14th, 1922.

The Identity of Geber. E. J. Holmyard (*Nature*, 1923, **111**, 191—193).—A criticism of Berthelot's view, now commonly held, that Geber's works are European forgeries of the thirteenth century; the author considers the identity of Geber with Jābir ibn Ḥaiyān (eighth century A.D.) to be extremely probable. A. A. E.

The Identity of Geber. J. R. Partington (*Nature*, 1923, **111**, 219—220; cf. preceding abstract).—An historical discussion in support of the probable authenticity of the Latin works ascribed to Geber. A. A. E.

Improved Optical Lever Manometer. Emmett K. Carver (*J. Amer. Chem. Soc.*, 1923, **45**, 59—63).—The optical lever manometer described by Shrader and Ryder (*Physical Rev.*, 1919, **13**, 321) has been slightly modified, whereby the sensitivity has been increased to 0·0001 mm. with an accuracy of about 0·0002 mm. of mercury. The modifications introduced are: a tube of 44 mm. diam. instead of narrow as in the original apparatus; this eliminates the error due to clinging of the mercury to the walls; a steel float instead of glass, which eliminates irregular wetting of the float; the knife edges are replaced by steel points, which prevent the changes which occur in the seating of the mirror support and so prevent a shift of zero; temperature changes were eliminated by placing the manometer in a thermostat with an optical glass window. J. F. S.

The Production of Coloured Flames for Use with Spectrophotometers and Polarimeters. J. J. Manley (*Phil. Mag.*, 1923, [vi], **45**, 336—337).—An apparatus is described for the introduction of aqueous solutions of salts, acidified with hydrochloric acid, into the Bunsen flame. This consists of a glass bulb of 20—30 c.c. capacity blown in the middle of a glass tube 1 cm. in diameter. The tube below the bulb is drawn out, bent at right angles, and cemented on to a vitrosil tube 5 mm. in diameter with a bore of 1 mm. Three or four platinum wires 0·3 mm. diameter are placed within the pipe of vitrosil, and constitute a wick extending out in a horizontal direction. The salt solutions when placed in the bulb are fed into the flame by capillary action along the platinum wires, and the rate of introduction can be adequately controlled by varying the inclination of the tube. W. E. G.

A Simple Automatic Apparatus for Delivering Drops and Keeping a Constant Level in Washing with Acids. Fritz Reimann (*Biochem. Z.*, 1922, **133**, 112—113).—An apparatus is described on the syphon principle which delivers a slow current of liquid drop by drop at a constant rate. W. O. K.

Inorganic Chemistry.

Active Chlorine. Y. VENKATARAMAIAH (*J. Physical Chem.*, 1923, **27**, 74—80).—Pure chlorine, prepared by heating gold chloride, was activated by the silent electric discharge, by electrical discharge at 20 mm. pressure, by ultra-violet light, or thermally. The active variety combines with ozone to form chlorine monoxide, with sulphur to form sulphur monochloride, with tellurium to form tellurium dichloride, and with benzene in the dark to form benzene hexachloride. It does not react with carbon, and is unstable above 50°. The activation of chlorine is accompanied by a contraction in volume, indicating that the activity is probably due to the presence of complex molecules. J. S. G. T.

Some Fundamental Atomic Weights. E. MOLES and J. M. CLAVERA (*Anal. Fís. Quím.*, 1922, **20**, 550—554).—Revised values are given for the atomic weights of fluorine (19·000), chlorine (35·457), bromine (79·926), nitrogen (14·008), carbon (12·000), and sodium (22·998). G. W. R.

A Class of Hydrates but little Stable, called Hydrates of Gases. A. BOUZAT (*Compt. rend.*, 1923, **176**, 253—255).—The author has calculated as accurately as possible the values of Q and q, the heats of formation of the hydrates from liquid water and solid water, respectively, in the cases of chlorine, bromine, and sulphur dioxide, and the values obtained give as the general formula for the hydrates $M,6H_2O$, which is in agreement with the experimental results and the hypothesis of Villard (A., 1897, ii, 151). W. G.

Solubility of Iodine Pentoxide in Sulphuric Acid. ARTHUR B. LAMB and A. W. PHILLIPS (*J. Amer. Chem. Soc.*, 1923, **45**, 108—112).—The solubility of iodine pentoxide has been determined at 24·77° in sulphuric acid of concentrations 50—106%, and is found to decrease up to 77% acid, and from this point upwards the initial solubility increases. However, a slow transformation of the solid phase begins at this point, with the formation of a less soluble solid substance. This substance has a maximum solubility at 104% acid. There is also evidence of a third solid substance in equilibrium with acids of intermediate concentrations. A possible explanation of these facts is that the main solubility curve (the initial curve) represents the solubility of iodic acid, whilst the second and probably the third curves represent solubilities of iodine pentoxide and of anhydro-iodic acid (HI_3O_8). J. F. S.

The Activation of Oxygen and Hydrogen Peroxide by Palladium Hydride. N. D. ZELINSKY and P. P. BORISSOW (*Ber.*, 1923, **56**, [*B*], 396—406).—The decolorisation of indigotin in faintly acid solution in the presence of palladium foil saturated with hydrogen occurs after the same time, whether air or oxygen is passed through the solution, although the production of hydrogen

peroxide is considerably greater in the latter circumstances. The amount of hydrogen peroxide, therefore, has little influence on the oxidation of indigotin.

The formation of hydrogen peroxide when air or oxygen is rapidly passed through water containing palladium foil thoroughly saturated with hydrogen takes place to a greater extent than has been previously supposed and attains a maximum concentration of 0·646 g. per litre. The oxidation of indigotin, however, under the experimental conditions cannot be attributed to this unexpectedly high concentration of hydrogen peroxide, since the effect is produced only after a much longer period by solutions of the technical agent of considerably greater concentration.

Decolorisation of indigotin proceeds much more rapidly under otherwise similar conditions in the absence of acid, and is observed when solutions of technical hydrogen peroxide and indigotin are brought into contact with palladium hydride and kept agitated by a current of carbon dioxide. Under these conditions, it is not possible for fission of the oxygen molecule or formation of a higher oxide of hydrogen to take place; the only possible explanation is to be found in the mutual action of palladium hydride and hydrogen peroxide.

Palladium hydride by itself has a marked reducing action towards indigotin; conversely, in the presence of hydrogen peroxide the oxidising action of the latter is catalytically accelerated by palladium hydride.

If air is passed through water in which palladium hydride is immersed and the latter is then removed, a solution is obtained which contains hydrogen peroxide, but is much more active towards indigotin than a solution of similar concentration which has been prepared from the technical peroxide. A similarly active solution can be obtained from palladium hydride, hydrogen peroxide, and carbon dioxide. If, however, the passage of the carbon dioxide is prolonged, the hydrogen peroxide is completely destroyed, and the solution does not react with potassium permanganate or zinc iodide-starch, even in the presence of ferrous sulphate; the activity is, however, rapidly restored by the addition of a little hydrogen peroxide. An active solution cannot be obtained from palladium and hydrogen peroxide, or from palladium hydride and water. The essential condition appears to consist of the presence of palladium hydride and hydrogen peroxide. The solution does not lose its activity when it is distilled, filtered, or preserved in a closed vessel during eight months. The presence of traces of palladium or of its compounds cannot be detected. Apparently, the effect is due to unusually minute traces of a substance with the properties of an inorganic peroxydase, which, for the present, cannot be detected analytically. The formation and decomposition of the possible compound may conceivably be expressed as follows: $Pd_3H_2+H_2O_2 \longrightarrow Pd_3H_2(OH)_2 \longrightarrow O+H_2O+Pd_3H_2$. The liberated oxygen atom affects the oxidation. This hypothesis explains the labile condition of hydrogen peroxide in the presence of palladium hydride. H. W.

Ozone and Allotropy. P. DE PAUW (*Chem. Weekblad*, 1923, 20, 26).—The conception of ozone as an allotrope of oxygen conflicts with the definitions of allotropy, since (1) both are gases, (2) their chemical reactions do not always yield identical products; the action of ozone on unsaturated organic compounds yields ozonides, which cannot be obtained from oxygen, (3) their solutions are not identical. Ozone, therefore, should not be selected as an example of allotropy; a more suitable example would be grey tin, which on heating passes over into the white form at constant temperature. S. I. L.

Forms of Sulphur in Coke. Physico-chemical Study of the Sulphur held by Carbon at High Temperatures. ALFRED R. POWELL (*J. Amer. Chem. Soc.*, 1923, 45, 1—16).—A phase-rule investigation of the carbon–sulphur complex which exists with carbon at high temperatures shows that the sulphur is present in two forms, adsorbed free sulphur and sulphur in solid solution in the carbon or held on the surface of the carbon in such a manner that it cannot be distinguished from a solid solution. Coke produced in the laboratory by heating coal rapidly contains sulphur in three forms, adsorbed free sulphur, sulphur in solid solution in the carbonaceous mass, or held on the surface in such a form as to exhibit all the properties of a solid solution and ferrous sulphide, together with much smaller quantities of calcium and magnesium sulphide. When this coke is maintained at a red heat for several hours, the adsorbed sulphur slowly passes into solid solution. Coke made by the usual commercial process of carbonisation over a comparatively long period contains, before it is cooled, only two forms of sulphur, sulphur in solid solution, as above, and ferrous sulphide with smaller quantities of other sulphides, the absorbed sulphur being absent or present in inappreciable quantities. When coke cools, even with limited access to the air, oxidation of ferrous sulphide takes place according to the equation $4FeS+3O_2=2Fe_2O_3+4S$. When coke is quenched as in ordinary coke manufacture, the decomposition of ferrous sulphide is incomplete; this is due to the speed with which the temperature of the coke is carried below that necessary for oxidation. Coke kept at a temperature about 500°, even with a limited supply of air, shows an almost complete oxidation of the ferrous sulphide. When hydrogen or gas containing hydrogen is led through red-hot coke in a coking oven, the sulphur removed as hydrogen sulphide comes from the decomposition of the ferrous sulphide, because this compound has the highest dissociation pressure of all the forms of sulphur in coke. J. F. S.

The Desulphuration of Metals by Lime. B. BOGITCH (*Compt rend.*, 1923, 176, 103—105).—If the metal is rich in sulphur a considerable amount of the sulphur is removed by calcium oxide at 1500—1600°, but if the sulphur content is low the desulphuration by lime or by a basic slag is extremely slow, and at this temperature the slag ceases to absorb sulphur when the sulphur content of the slag reaches about 22%, although there may still be some unaltered

calcium oxide present. If the proportion of calcium fluoride in the slag is increased, the absorption of sulphur continues until the whole of the oxide is converted into sulphide. W. G.

Vapour Pressures of Sulphur Dioxide. W. MUND (*Bull. Acad. roy. Belg.*, 1919, [v], **5**, 529—543).—The author has determined, by the static method, the vapour pressures of sulphur dioxide corresponding with temperatures between $-42°$ and $0°$. The errors common to such determinations are examined and eliminated by methods for the description of which the original paper should be consulted. The vapour pressure of sulphur dioxide at 0° was found to be 1163·98 mm. or 1·53 atmos., other determinations being made at the temperature of fusion of certain eutectic mixtures (cf. Bruylants and Mund, *ibid.*, 113). E. E. T.

Acidity and Electrolytic Dissociation of Hydrogen Selenide. M. DE HLASKO (*Bull. Acad. Polonaise Sci. Lettres*, 1921, [*A*], 18—25; from *Chem. Zentr.*, 1923, i, 16).—The equivalent conductivity of the ion HSe′, calculated by the Kohlrausch formula, from measurements of the conductivity of aqueous solutions of hydrogen selenide is 70. The value $1{\cdot}88\times10^{-4}$ was obtained for the dissociation constant of hydrogen selenide. G. W. R.

Selenium Nitride. WILHELM STRECKER and LUDWIG CLAUS (*Ber.*, 1923, **56**, [*B*], 362—383).—Selenium nitride, SeN, has been obtained previously as an amorphous, pale orange-yellow, extremely explosive powder by the action of gaseous ammonia on a number of compounds of selenium. In the hope of securing a better-regulated course of the change, the action of liquid ammonia has now been investigated.

The action of liquid ammonia on diselenium dichloride is exceedingly vigorous, and results in the deposition of red selenium; a similar result is obtained if the chloride is mixed with chloroform or anhydrous benzene, only traces of the nitride being produced. In ethereal solution, on the other hand, a pale brown, amorphous *compound*, Se_2NCl, is formed. Selenium tetrachloride in the absence of solvent behaves similarly to the lower chloride towards liquid ammonia; in the presence of carbon disulphide it is converted into a pale yellow, amorphous material which could not be satisfactorily purified. Selenyl chloride is transformed by liquid ammonia in the presence of ether in open vessels into the primary *product*, $SeOCl_2,4NH_3$, which is decomposed by water into selenium, selenium nitride, ammonium chloride and selenite, and selenious acid, whereas in a sealed tube it gives selenium nitride in comparatively good yield.

Diselenium dibromide reacts with gaseous ammonia in the same manner as the corresponding chloride; with liquid ammonia in the presence of ether, it gives the *compound*, Se_2N_2Br. The reaction of selenium tetrabromide towards liquid ammonia resembles closely that of the tetrachloride. On the other hand, the action of these substances in the presence of carbon disulphide proceeds more quietly than when the chloride is used, and gives

better yields of the nitride. The change follows a similar course in the presence of benzene.

It therefore appears that the selenium tetrahalides are the best initial materials for the preparation of selenium nitride; the small amounts of the latter which are produced when the lower halides or the oxy-compounds are employed appear to be derived from intermediately formed tetrahalide.

Selenium nitride is an amorphous, orange-coloured powder which is considerably more sensitive than mercury fulminate to shock or blow; it explodes with certainty when heated at 160°. According to Verneuil, its formation from the tetrachloride and ammonia is expressible by the equation: $3SeCl_4+16NH_3=3SeN+12NH_4Cl+N$. In the case of the bromide in the presence of carbon disulphide, the volume of nitrogen evolved is far in excess of that required by a similar equation, whereas in the presence of benzene the reaction $3SeBr_4+16NH_3=2SeN+Se+N_2+12NH_4Br$ appears to take place.

Chlorine and bromine react explosively with selenium nitride. In the presence of carbon disulphide, the action of bromine leads to the formation of a brownish-green, hygroscopic *substance*, SeN_2Br_4. Bromine vapour diluted with carbon dioxide transforms solid selenium nitride into ammonium selenohexabromide, $(NH_4)_2SeBr_6$, the formation of which appears to be due to the action of atmospheric moisture on a primary additive product of bromine and the nitride. Chlorine, in similar circumstances, gives the *product* $SeNCl_3$. Bromination of the compound Se_2N_2Br yields the substance SeN_2Br_4, whereas exhaustive chlorination of the product Se_2NCl yields Se_2NCl_6, which possibly is not quite homogeneous.

Selenium nitride is not affected by solid iodine or by a solution of the halogen in ether or chloroform.

The constitution of selenium nitride is discussed at some length; unfortunately, a suitable solvent is not available for the determination of the molecular weight, but reasons are advanced in favour of a cyclic structure of the molecule Se_4N_4.

The possibility that selenium nitride is a derivative of azoimide has been examined, but this does not appear to be the case. Diselenium dibromide reacts with silver azide suspended in benzene with the formation of silver chloride and selenium; similar changes occur with lead and sodium azides. Selenium tetrabromide and silver azide give a pale yellow compound, which becomes bluish-black when exposed to light. Selenium oxychloride and sodium azide in the presence of benzene gives nitrogen and the *compound* $2NaCl,SeO_2,H_2O$. H. W.

New Method of Determination of the Atomic Weight of Tellurium. P. Bruylants and J. Michielsen (*Bull. Acad. roy. Belg.*, 1919, [v], **5**, 119—130).—The ratio $Te:H_2$ and $Te:H_2O$ have been measured. Hydrogen telluride, prepared by the electrolysis of dilute sulphuric acid, using a tellurium cathode, was purified by fractional distillation, etc., from the accompanying hydrides

of sulphur, selenium, and antimony, and decomposed into its elements at a temperature of 200—220°. The tellurium was weighed as such, and the hydrogen oxidised to water by means of cupric oxide. A marked difference obtained between the ratio Te : H_2 measured directly, and that measured indirectly through water, was traced to incomplete decomposition of the hydrogen telluride, and, correcting for this, the authors obtain the figure 127·8 for the atomic weight of tellurium. E. E. T.

The Allotropy of Tellurium. A DAMIENS (*Ann. Chim.*, 1922, [ix], **18**, 282—312).—A detailed description of work which has been previously published (A., 1922, ii, 498, 562). The general conclusion is drawn that the analogy between the allotropy of sulphur and tellurium cannot be accepted, as the latter element is clearly differentiated by the existence of a single crystalline form. H. J. E.

Properties of Hydrogen Telluride. P. BRUYLANTS (*Bull. Acad. roy. Belg.*, 1920, [v], **6**, 472—478).—Pure hydrogen telluride was prepared by a modification of the process used previously Bruylants and Michielsen, *ibid.*, 1919, 119—130; this vol., ii, 153), and various constants were determined. The triple point has for co-ordinates t −45·4°, p 102 mm. The density is d^0 2·65. The vapour-pressure curve was compared with the curves for ethyl alcohol and carbon disulphide, whence the b. p. at 760 mm. was calculated as −2·2°, using the Ramsay-Young equation. The actual b. p. found by experiment was −1·8°. The calculated latent heat of vaporisation was found to be L 5·7 cal., whence, by Trouton's Rule, $L/T=20·9$. The critical temperature of the hydride lies in the region of 200°, if the Guldberg-Guye relation holds. E. E. T.

Acidity of Hydrogen Telluride. Electrolytic Dissociation of Hydrogen Telluride. M. DE HLASKO (*Bull. Acad. Polonaise Sci. Lettres*, 1919, [*A*], 73—78; from *Chem. Zentr.*, 1923, **i**, 15—16).—The electrical conductivity of aqueous solutions of hydrogen telluride was determined. The value 61 was obtained for the equivalent conductivity of the ion HTe′. The value $K=2·27\times10^{-3}$ was obtained for the dissociation constant of hydrogen telluride in aqueous solution. G. W. R.

The After-glow of Activated Nitrogen. MARCELLO PIRANI and ELLEN LAX (*Wiss. Veröffentl. Siemens-Konzern*, 1922, **2**, 203—207; from *Chem. Zentr.*, 1923, i, 17; cf. A., 1921, ii, 197—198).—Highly purified nitrogen in sealed glass vessels was submitted to high frequency discharge of about 100,000 periods per second. The discharge occurs in the form of bright threads joining up with the walls of the vessel. At pressures varying from 2—700 mm. with an optimum at 60—200 mm., a pale blue glow was produced. Contamination by gas given off from the walls of the vessels during discharge amounted to less than 5×10^{-5}%. In experiments at pressures of 150 to 180 mm., nitrogen always showed luminescence either at once or after longer discharge (ten minutes). The glow

spreads from those parts of the walls of the vessels receiving the greatest impact of electrons. The luminescence occurs when the nitrogen is contaminated with gases evolved from the hygroscopic moisture on the glass walls of the vessels. These may amount at 150 mm. pressure to 10^{-5} to 10^{-4}%. Inert gases and electropositive gases such as hydrogen have little effect. Electronegative gases such as oxygen, water vapour, and iodine vapour give in concentration of about $1{\cdot}5 \times 10^{-3}$ a maximum after-luminescence; with 6 to 8×10^{-3}%, the luminescence is inhibited. Perfectly pure nitrogen does not show luminescence. It is supposed that an active form of nitrogen is produced which decomposes in the presence of small quantities of electronegative gases with emission of light. Electronegative gases increase the point discharge and thereby the number of active molecules and the rate of decomposition. With larger amounts of impurity, the point discharge is decreased whilst the rate of decomposition is so much increased that luminescence only occurs in the region of the lines of discharge. With still greater quantities of impurity, for example, 10^{-2}% of oxygen, the decomposition within the region of the lines of discharge is so rapid that luminescence is no longer visible.

G. W. R.

The Catalytic Oxidation of Ammonia by Air in Contact with Platinum. EUGÈNE DECARRIÈRE (*Ann. Chim.*, 1922, [ix], 18, 312—388).—A detailed description of work previously published. Fuller particulars are given of the author's work of the action on the catalyst of certain gaseous impurities (A., 1921, ii, 503, 546; 1922, ii, 284) and also of work carried out in collaboration with Pascal on the effect of variations in the form of the catalyst (A., 1919, ii, 463).

H. J. E.

The Crystal Structure of Hydrazine Dihydrochloride. RALPH W. G. WYCKOFF (*Amer. J. Sci.*, 1923, 5, 15—22).—Using Laue photographic and spectrographic data, the structure of hydrazine dihydrochloride has been shown to be based on the paramorphic hemihedry of the cubic system. The crystal unit consists of a cell, 7·89 Å. in length, containing four chemical molecules. An approximate placing of the atoms in the unit cube has been made, and the arrangement is analogous to that obtaining in crystals of the alkaline-earth nitrates, the hydrazine groups occupying positions analogous to those held by the alkaline-earth metals, and the chlorine atoms replacing the nitrate groups. The distance between adjacent chlorine atoms is approximately 3·96 Å.; between chlorine and nitrogen atoms, about 3·14 Å. These results are at variance with the hypothesis of constant atomic radii.

W. E. G.

The Preparation of Hydroxylamine Hydrochloride and Acetoxime. WALDO L. SEMON (*J. Amer. Chem. Soc.*, 1923, **45**, 188—190).—A modification of Divers's method (T., 1896, **69**, 1665), in which the conversion of the sodium carbonate first into a mixture of hydrogen carbonate and hydrogen sulphite and then

into hydrogen sulphite alone is carried out prior to the addition of the sodium nitrite, as a result of which the time required for the complete operation and the amount of cooling necessary are considerably reduced. Further, the sodium hydroxylaminedisulphonate is converted directly into acetoxime (cf. Raschig, A., 1887, 549, 635) and this is then hydrolysed by hydrochloric acid and the required hydroxylamine hydrochloride obtained after distilling off the acetone (cf. Janny, A., 1883, 580, 581). Under these conditions, a product is obtained free from ammonium salts and with a yield of 53—77%. W. G.

Black Colloidal Suspensions in Phosphorus. CLAUDE HAINES HALL, jun. (*J. Amer. Chem. Soc.*, 1923, **45**, 67—69).—The literature relating to black phosphorus is quoted and discussed, and it is shown that Thénard's black phosphorus is a colloidal suspension of mercury in the phosphorus, whilst the black phosphorus obtained by Bridgman (A., 1914, ii, 647) is a true allotropic modification of phosphorus. Using Svedberg's method of colloidisation, the author has dispersed copper and mercury in molten phosphorus to form colloidal suspensions of these metals. The material obtained with copper and mercury was homogeneous, readily inflammable, and had *d* 1·9. When extracted with carbon disulphide, tiny, black crystals of copper phosphide were obtained in the case of copper, but with mercury droplets of mercury; a few red flakes of amorphous phosphorus were obtained in each case. J. F. S.

Action of Light on Arsenic Trisulphide Hydrosol. RAY V. MURPHY and J. HOWARD MATHEWS (*J. Amer. Chem. Soc.*, 1923, **45**, 16—22).—The effect of exposing arsenic trisulphide sols of varying concentrations to the light of a condensed filament lamp for various periods at constant temperature has been investigated by measuring the electrical conductivity of the solutions after each exposure. The results show that the electrical conductivity increases on exposing the sols to light, the rate of change increasing with decreasing concentration of the colloid. This is explained as due to the increased photochemical activity of the colloid per unit mass of arsenic trisulphide, brought about by the greater dispersion of the more dilute sol. The reaction is explained, according to the suggestion of Freundlich and Nathansohn (A., 1921, ii, 494), as one of a two-stage photochemical oxidation of hydrogen sulphide to colloidal sulphur and a thionic acid, accompanied by a reaction between hydrogen sulphide and the thionic acid, which serve as stabilising electrolytes for the micellæ of arsenic trisulphide and sulphur, respectively. Removal of the stabilising electrolytes produces a de-stabilisation of the two colloids which are consequently precipitated. The increase in electrical conductivity is explained as due to the building up of a concentration of the thionic acid sufficient to serve as the stabilising electrolyte for the colloidal sulphur, the reaction between hydrogen sulphide and the thionic acid then proceeding at such a rate that the equilibrium is maintained between the several components of

the system, further change in the electrical conductivity thus being prevented. J. F. S.

Estimation of the Atomic Weight of Boron. Alfred Stock and Ernst Kuss (*Ber.*, 1923, **56**, [*B*], 314—316).—A preliminary account. The full details of the work will be published elsewhere.

The method adopted consists in the decomposition of weighed amounts of diborane, B_2H_6 (cf. Stock and Massenez, A., 1913, ii, 44), by water in accordance with the equation $B_2H_6+6H_2O=2H_3BO_3+6H_2$, and measurement of the evolved hydrogen. As mean value of six determinations, the atomic weight of boron is found to be 10·8055 (H=1·0077), the mean error of the individual experiments being ±0·0036 and of the average value ±0·0015. The figure is slightly lower than that obtained (10·82—10·84) from the analysis of boron trichloride by Hönigschmid and by Baxter and Scott, but agrees with that predicted by Aston (10·75±0·07) from observations of the mass spectrum.

The atomic weight of silicon has been estimated similarly by decomposing monosilane with sodium hydroxide. Preliminary results are 28·15, 28·16, and 28·14, which, however, are given with reserve. It is certain that the usually adopted figure for the atomic weight of silicon (28·3) is considerably too high. H. W.

Absorption of Carbon Monoxide by Cuprous Ammonium Carbonate and Formate Solutions. Alfred T. Larson and Clark S. Teitsworth (*J. Amer. Chem. Soc.*, 1922, **44**, 2878—2885).—A static method for investigating the absorption capacity of liquid absorbents for carbon monoxide is described, and has been used with various solutions of cuprous ammonium formate and cuprous ammonium carbonate for this purpose. It is shown that for equivalent concentrations the formate and carbonate solutions have essentially the same absorption capacity for carbon monoxide under the same conditions of temperature and partial pressure of carbon monoxide. At low temperatures (0°), the results indicate the formation of a complex or additive compound containing 1 mol. of carbon monoxide per mol. of copper, which is largely decomposed at slightly elevated temperatures (60°). Small variations in the concentration of total carbonate or formate have no appreciable effect on the solubility of carbon monoxide, but the solubility is proportional to the copper concentration of the solution. The carbonate solutions are much less stable than the formate solutions; the former deposits copper at 60°. The maximum permissible copper concentration of any solution is fixed by the temperature at which the solution is to be regenerated. High copper concentration is accompanied by increased precipitation of free copper as the temperature is raised. High pressures of carbon monoxide also tend to increase the precipitation of copper. Solutions of cuprous ammonium formate are preferable to cuprous ammonium carbonate, because the deposition of copper at the regeneration temperature is very much less. J. F. S.

Formation of Carbon Disulphide by the Action of Sulphur Dioxide on Carbon. B. RASSOW and K. HOFFMANN (*J. pr. Chem.*, 1922, [ii], **104**, 207—240).—When sulphur dioxide is led over red-hot carbon, the following reactions can occur: (i) $2SO_2+2C=2CO_2+S_2$. (ii) $S_2+C\rightleftharpoons CS_2$. (iii) $CO_2+C\rightleftharpoons 2CO$. (iv) $S_2+2CO_2\rightleftharpoons COS+CO+SO_2$. (v) $S_2+2CO\rightleftharpoons 2COS$. (vi) $CS_2+CO_2\rightleftharpoons 2CO+S_2\rightleftharpoons 2COS$. (vii) $2SO_2+4C\rightleftharpoons 4CO+S_2$. The mutual influence of these reactions and the influence of temperature are discussed in detail, the conclusion being that an increase in the reaction temperature can lead only to an optimum formation of carbon disulphide. This prediction has been verified experimentally.

Sulphur dioxide was led over red-hot beechwood charcoal previously freed from hydrogen by heating in a current of chlorine. Free sulphur in the issuing gas was collected by condensation and filtration through glass wool; carbon disulphide vapour was next absorbed by means of ethereal triethylphosphine, the precipitated additive product being collected and weighed. Carbon dioxide and carbon oxysulphide were absorbed in ammoniacal calcium chloride solution, the total carbon in the liquid being determined by oxidation with hydrogen peroxide, followed by filtration and titration of the precipitated calcium carbonate, whilst the sulphur in the filtrate was estimated as barium sulphate. The remaining gas was finally collected over water, and the carbon monoxide estimated in the usual way.

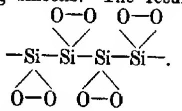
At 700°, only traces of carbon disulphide are produced; the amount formed increases with rising temperature, the product containing also carbon oxysulphide, carbon dioxide, free sulphur, and small amounts of carbon monoxide. The maximum formation of carbon disulphide occurs at 850—900°, the sulphur from the sulphur dioxide being then distributed as follows: 35% as carbon disulphide, 55% as carbon oxysulphide, and 10% as free sulphur, whilst carbon monoxide and a small amount of carbon dioxide constitute the rest of the gas mixture. Above 900°, the proportion of free sulphur increases at the expense of both carbon disulphide and carbon oxysulphide; the oxygen from the sulphur dioxide appears almost exclusively as carbon monoxide. Above 1100°, free sulphur and carbon monoxide are the only products. The formation of carbon oxysulphide decreases continuously with increasing temperature; the free sulphur produced is a minimum at about 850°.

It is concluded that the process is useless as a technical method of making carbon disulphide. W. S. N.

Absorption of Carbon Disulphide Vapour by Aqueous Solutions of Sodium Trinitride [Azide]. A. J. CURRIER and A. W. BROWNE (*J. Amer. Chem. Soc.*, 1922, **44**, 2849—2854).—The absorption of carbon disulphide vapour from gaseous mixtures by solutions of sodium azide in water has been investigated. It is shown that a 1% solution of sodium azide absorbs the theoretical amount of carbon disulphide vapour from gaseous mixtures, but that a further amount may also be absorbed at a much slower

rate. The absorption of carbon disulphide by a 1% aqueous solution of sodium azide amounts to about 3·5 times the volume of the absorbing liquid, and takes place irreversibly with the quantitative formation of sodium azidodithiocarbonate, $NaN_3+CS_2=NaS{\cdot}CSN_3$. Various mixtures of carbon disulphide vapour with air, oxygen, nitrogen, hydrogen, methane, and carbon monoxide have been analysed, using a 5% or a saturated aqueous solution of sodium azide as absorbent with exceedingly good results. The solution of the salt produced by the interaction of the absorbent and vapour has been found to possess no dangerously explosive properties, but to decompose very slowly after keeping for long periods, with the formation of nitrogen, sulphur, and sodium thiocyanate. J. F. S.

A Theory of the Structure and Polymorphism of Silica. ROBERT B. SOSMAN (*J. Franklin Inst.*, 1922, **194**, 741—764).—A set of hypotheses is put forward to explain in a consistent manner the wide variety of experimental data on the modifications of silica. It is assumed that the silica atom triplet, SiO_2, maintains its individuality in all the forms of quartz and silicates, and that the silica molecules aggregate themselves in chains in which the silicon atoms share a pair of electrons with each oxygen, and the oxygen atoms share a pair of electrons between them. At the same time, the silicon shares one pair of electrons with each of two neighbouring silicons. The resulting silica thread possesses the constitution



. These threads form in the liquid state or even in the vapour. In the liquid they are in a constant state of vibration and movement, with the oxygen atoms in haphazard orientation relative to the thread. On this view, solid silica glass is analogous to a compressed pad of wires. The thread structure is believed to persist in the crystalline state, and the three principal crystalline modifications (cristobalite, tridymite, and quartz) are built up by combining the threads through the oxygen atoms. The high to low inversions (α—β) in all three forms are considered to be due to a change in the state of motion of certain electron orbits resulting from increased thermal vibration of the atoms. These changes produce sudden alterations in the shape of the silica triplet and the relative positions of the two oxygen atoms. In cristobalite, the oxygen atoms of the silica threads are incompletely fixed, some of the threads being capable of rotation about the silica axis. This explains the variable inversion point of this form of quartz. The theory of the polymorphism of silica is extended to silicate systems, and to the oxides of other elements in group IV of the periodic classification. This view of the structure of the silica complex is in agreement with the minimum in the temperature volume curve of silica glass, and the relations between the specific heats of the various forms of quartz.

W. E. G.

Silicon Hydrides. XII. Disiloxan, $(SiH_3)_2O$. ALFRED STOCK and CARL SOMIESKI (*Ber.*, 1923, **56**, [*B*], 132—135).—Unsuccessful attempts are described to convert disiloxan (Stock, Somieski, and Wintgen, A., 1918, ii, 110) into disilene, Si_2H_4.

Disiloxan is not sensibly affected when heated at 300°; at 400°, it yields small amounts of hydrogen, monosilane, and polymeric prosiloxan, but the greater portion of the original substance remains unchanged. Phosphoric oxide decomposes disiloxan at the atmospheric temperature, giving a little hydrogen, much monosilane, and polymeric prosiloxan. The initial reaction appears to consist in a slight hydrolysis in accordance with the equation $(SiH_3)_2O+H_2O=2SiH_2O+2H_2$, followed by a polymerisation of the volatile prosiloxan to its non-volatile polymeride. The liberated hydrogen is largely utilised in the reduction of disiloxan to monosilane, $(SiH_3)_2O+2H_2=2SiH_4+H_2O$. The water which is thus set free hydrolyses a further quantity of disiloxan, and thus the change continues until it is brought to a gradual conclusion by the absorption of water by the excess of dry phosphoric oxide. H. W.

Silicon Hydrides. XIII. Some Reactions of Chloromonosilane and Disilane. ALFRED STOCK and CARL SOMIESKI (*Ber.*, 1923, **56**, [*B*], 247—252).—Disilane is very stable towards heat, but at not too high a temperature (about 500°) suffers decomposition which resembles the cracking of hydrocarbons. In addition to silicon, large volumes of monosilane are obtained, the production of which depends on the reducing action of primarily liberated hydrogen on unchanged disilane. Higher hydrides are not produced in sufficient quantity to make the method practicable for their preparation. At a higher temperature, the fission of disilane into silicon and hydrogen predominates.

Chloromonosilane and silver cyanide at 150° yield hydrogen cyanide and cyanogen as gaseous products. At 300°, chloromonosilane is decomposed by silver sulphide into non-volatile silicon compounds, hydrogen, and hydrogen sulphide. Monochlorosilane and hydrogen sulphide at 150° in the presence of aluminium chloride give hydrogen, dichloromonosilane, and a volatile compound containing sulphur [possibly $SiH_3{\cdot}SH$ or $(SiH_3)_2S$], which has not been investigated completely.

The main products of the action of sodium amalgam on dichloromonosilane are monosilane and the unsaturated, yellow, polymerised hydride, $(SiH)_x$. The course of the reaction is represented by the equations $SiH_2Cl_2+4Na=SiH_2Na_2+2NaCl$; SiH_2Na_2+ mercury $\longrightarrow SiH_2+$sodium amalgam; $3SiH_2 \longrightarrow SiH_4+2(SiH)_x$.

The following tensions have been measured for hydrogen sulphide prepared from iron sulphide and hydrochloric acid and purified by fractional distillation in a vacuum: −130°, 3 mm.; −120°, 7 mm.; −110°, 20 mm.; −100°, 54 mm.; −90°, 117 mm.; −80°, 247 mm.; −70°, 440 mm.; −59·1°, 778 mm. The pure dry gas can be preserved unchanged over mercury. H. W.

The Densities of Dilute Solutions of Potassium Salts and the Volume Changes Occurring on Solution. HAROLD HARTLEY and WILLIAM HENRY BARRETT (T., 1923, **123**, 398—401).

The Formation of Pyramidal Crystals by Alkali Halides. HERMANN KUNZ-KRAUSE (*Ber. Deut. pharm. Ges.*, 1922, **32**, 329—334).—The crystallisation of sodium chloride in pyramidal crystals previously observed from time to time by various workers has been shown to take place also with potassium iodide. Photographs are shown of such crystals of both these salts, and their mode of formation is indicated by diagrams of crystal growth at the surface of a saturated solution. P. M.

The Preparation of Potassium Hydroxylamine*iso*disulphonate. F. RASCHIG (*Ber.*, 1923, **56**, [*B*], 206—208).—The preparation of potassium hydroxylamine*iso*disulphonate,

$$SO_3K{\cdot}NH{\cdot}O{\cdot}SO_3K,$$

has previously been a matter of some difficulty, mainly owing to the poor yields and unstable nature of the intermediately formed trisulphonate. A convenient process for preparing the latter is now described.

Sodium hydrogen sulphite solution (5N, 1200 c.c.) is added with continuous stirring to a mixture of ice (1000 g.) and technical sodium nitrite (150 g.), whereby the temperature is not allowed to rise above 5°. One c.c. of the solution, when tested after the addition has been finished for ten minutes, should react with about 17 c.c. of N/10-iodine solution, and subsequently require 14—15 c.c. of N/10-sodium hydroxide for neutralisation in the presence of methyl-orange. Any ice particles are removed and the solution is treated whilst being vigorously shaken with lead peroxide (600 g.). It is subsequently warmed on the water-bath, frequent agitation being required to prevent the oxidising agent from becoming aggregated. The conclusion of the oxidation is reached when 1 c.c. of the solution neutralises about 9 c.c. of N/10-hydrochloric acid and subsequently does not react with more than 1 c.c. of N/10-iodine solution. The solution is filtered and the residue washed with hot water (200 c.c.). The filtrate is warmed with technical potassium chloride (800 g.) until the precipitated lead chloride forms coarse particles, which are removed. The filtrate, after remaining for three days in an ice-chest, deposits potassium hydroxylaminetrisulphonate (790 g.) in large monosymmetric prisms. It is filtered, dried on porous earthenware, and subsequently over calcium chloride. The finely-divided, dry salt (423 g.) is agitated with boiling water (800 c.c.) containing 1 c.c. of dilute hydrochloric acid until solution is complete; the small amount of lead sulphate which separates is removed. The filtrate deposits potassium hydroxylamine*iso*disulphonate in colourless crystals, the yield being about 90% of that theoretically possible. H. W.

The Alkali Permanganates. M. CRESPI and E. MOLES (*Anal. Fis. Quim.*, 1922, **20**, 555—562).—The alkali permanganates, with the exception of sodium permanganate and ammonium permanganate, which are relatively unstable, decompose at temperatures which increase almost proportionally to their molecular weights. The densities are closely correlated with molecular weights. The thermal decomposition is similar throughout the series, and is

represented, for example, in the case of potassium permanganate, by the equation $10KMnO_4 = 2K_2MnO_3 + (3K_2MnO_4, 5MnO_2) + 6O_2$.

G. W. R.

The Dissociation of Potassium Chloroiridiate. G. GIRE (*Compt. rend.*, 1923, **176**, 241—244).—The author has studied the decomposition of potassium chloroiridiate in the same manner as that used for barium chloroplatinate (A., 1922, ii, 551), and from his results calculates the heat of fusion of a molecule of potassium chloride to be −4·92 cal., which is in close agreement with the value obtained by Schemtschuschny and Rambach (A., 1910, ii, 204). W. G.

Molecular Weight of the Sodium–Tellurium Complex in Liquid Ammonia as Derived from Vapour Pressure Measurements. CHARLES A. KRAUS and EDWARD H. ZEITFUCHS (*J. Amer. Chem. Soc.*, 1922, **44**, 2714—2728).—The lowering of the vapour pressure of liquid ammonia, at temperatures of 17·9° to 20°, due to the complex sodium-tellurium compound, has been measured at a series of concentrations down to 0·03N. It is shown that when the values of $\Delta P/P$ are plotted against the values of $n/n+N$, where n is the number of atoms of sodium in the mixture, a curve is obtained which, for dilute solutions, approaches very closely to a straight line, and for which the value $(\Delta P/P) / (n/n+N)$ is equal to 0·5. Apparently solutions of the complex telluride in liquid ammonia very nearly follow Raoult's law; and from the value of the above ratio it follows that two atoms of sodium are present in each molecule of the complex telluride present in the solution. The complex telluride-ion, therefore, carries two negative charges. The formation of the complex telluride consists in the addition of tellurium atoms to the normal telluride-ion, the valency of the telluride-ion undergoing no change under these conditions. The bearing of this result on the present-day conceptions of the nature of other complexes in ammonia solution and of metallic alloys in general is discussed. J. F. S.

The Position of the Atoms in the Optically Active Crystals, $NaClO_3$ and $NaBrO_3$. L. VEGARD (*Z. Physik*, 1922, **12**, 289—303).—By the employment of the Debye powder method, the positions of the atoms in the chlorate and bromate crystals have been determined. The parameter values lead to a very simple grouping of the atoms in space which is in agreement with the volume conditions. As was recognised by Bragg, the space lattices are based on the face-centred cube, but none of the atom centres themselves lies in a face-centred arrangement. The atoms lie about trigonal axes, with the halogen and the three oxygen atoms forming a pyramid group. The halogen, which forms the apex of this group, is attached to a sodium atom along the vertical axis of the pyramid. Each oxygen atom is in contact with two other oxygen atoms, and the halogen atom in the same molecule, and with two sodium atoms from neighbouring molecules. The halogen atom is not in contact with the sodium atom. The following distances

obtain between the atoms in contact, $D_{Na-O}=2·36$ Å.; $D_{Br-O}=1·89$ Å.; $D_{O-O}=1·20$ Å., whereas, according to Bragg, these distances should be 2·42 Å., 1·84 Å., and 1·30 Å., respectively. The arrangement of the oxygen atoms is quite different from that ascribed to them by Koltmeijer, Bijvoet, and Karssen (*K. Akad. Wetensch. Amsterdam*, 1921, **23**, 644—653). The intensities of the lines calculated on the basis of the above structure is, however, in agreement with the experimental values.

Both the chlorine and sodium atoms are displaced towards the angles of the unit cube, and this involves a rotation of the pyramid group about the pyramidal axis. Since this rotation can occur in two directions, the occurrence of optical activity is accounted for. This rotation does not occur in the isomorphous group of nitrates, although these crystallise in the same system as the chlorate and bromate. These substances are, however, inactive. Formulæ based on the assumption that contact between the atoms in the crystal indicates the positions of the valency forces are not in accordance with chemical ideas. It is therefore concluded that crystal structure gives very little clue to chemical constitution. The volume conditions governing the packing of the atoms in the crystal, and not the chemical forces, are the deciding factor in the atomic arrangement. W. E. G.

The System Sodium Sulphate–Sodium Chromate–Water. II. YUKICHI OSAKA and RYOHEI YOSHIDA (*Mem. Coll. Sci. Kyoto*, 1922, **6**, 49—54).—This work is a continuation of that of Takeuchi (A., 1916, ii, 31), and the equilibrium of the sodium sulphate–sodium chromate system has now been studied at 28°, 31°, and 33°. At 28° and 31°, the chromate exists as tetrahydrate and its solubility in the sulphate as decahydrate decreases as the temperature rises, the molar fraction being 0·16 at 28° and 0·04 at 31°. The solid solution obtained by Takeuchi at 25° having the composition $2Na_2SO_4,Na_2CrO_4,30H_2O$ was not a definite compound. At 33°, no solid solution of the decahydrates exists.

E. H. R.

Some Slags from the Clausthal Silver Furnaces. A New Family of Silicates of Composition $R_3Si_2O_7$. KURT HOFMANN-DEGEN (*Sitzungsber. Heidelberger Akad. Wiss.*, 1919, [A. 14]; from *Chem. Zentr.*, 1922, iii, 1248—1249).—Cavities of slag from the Clausthal silver works contain a zinc bearing iron–calcium olivine (Fe_2SiO_4 50·9%, Zn_2SiO_4 2·7%, Mg_2SiO_4 5·1%, Ca_2SiO_4 41·2%) having $a:b:c=0·4371:1:0·5768$, and refractive indices γ_D 1·7430, β_D 1·7340, and α_D 1·6958, and also a tetragonal silicate mineral called "justite." *Justite* has the composition $(Mg,Fe,Zn,Mn,Ca)_3Si_2O_7$, where Ca : (Mg,Fe,Zn,Mn)=1 : 1. Its refractive indices are $\epsilon_D=1·6581$ and ω_D 1·6712. It resembles the naturally occurring hardystonite, $(Ca,Zn)_3Si_2O_7$. A slag from Bochum consisted of tetragonal crystals of the composition $(Ca,Mg,Fe,Mn)_3Si_2O_7$, where Ca : (Mg,Fe,Mn)=2 : 1. The tetragonal slag silicates including hardystonite form a well-defined isomorphous group of the type $R_3Si_2O_7$. G. W. R.

Binary Lead Alloys. J. GOEBEL (*Z. Metallk.*, 1922, **14**, 357—366, 388—394, 425—432, 449—456).—The hardness and density of alloys of lead with sodium, magnesium, arsenic, antimony, cadmium, tin, mercury, and bismuth have been determined. The hardening effect of small quantities of these elements decreases in the order named. Very small quantities of sodium and magnesium have a considerable effect in increasing the hardness of lead, the solid solution of sodium in lead containing about 1% of sodium having a Brinell number of 35 against 5 for pure lead (cf. *J.S.C.I.*, 1923, March). A. R. P.

Topochemical Processes. The Conditions of Formation and the Forms of Lead Oxide. V. KOHLSCHÜTTER and H. ROESTI (*Ber.*, 1923, **56**, [*B*], 275—288).—The formation of the yellow and red modifications of lead oxide during the course of the following reactions has been studied: (i) precipitations in which a change in the nature of the product may be expected as a consequence of alteration of the temperature, concentration, and nature of the solution; (ii) the oxidation of metallic lead beneath water by oxygen; (iii) the pseudomorphic transformation of solid lead salts; (iv) the thermal decomposition of compounds of lead oxide, and (v) the oxidation of lead vapour and rapid condensation of the product.

The yellow variety of lead oxide is produced when the compound is immediately formed from molecular solutions or by the oxidation of lead vapour. On the other hand, the red modification is obtained by reactions in which water plays a part through the hydrate, $3PbO,H_2O$, and thus through a solid compound. This reaction is observed only when the hydrate is in a suitably disperse condition in which a certain spatial compression appears to be essential; it does not occur with the recognisably crystalline hydrate. The process therefore involves a well-marked topochemical factor. The formation of the red variety by the thermal decomposition of lead oxide or hydrate can be explained from the same point of view, if it is assumed that the oxide molecules, after rupture of the molecules, more readily form complexes by reason of their proximity to one another than they arrange themselves to the elements of the yellow variety which is favoured by separation from solution or from the gaseous phase.

The formation of the red variety through the hydrate appears to indicate a difference in the complexity of the molecules of the two forms. The assumption is made that the condensed molecule which is already present in the hydrate, $3PbO,H_2O$, remains intact during the formation of the red oxide. When, therefore, the latter is produced by the dissociation of a solid compound, a coalescence of several molecules must have occurred which is favoured by topochemical conditions. In solution, on the other hand, the simple lead hydroxide, $Pb(OH)_2$, is present, and hence a simpler molecular formula may be assigned to the yellow lead oxide obtained therefrom.

The simultaneous production of the two oxides from solution

depends on the dehydration and amphoteric ionisation of the bivalent metallic hydroxide (cf. von Euler, A., 1922, ii, 831, who has discussed the analogous case of copper hydroxide). The production of the yellow variety is due to the dehydration of lead hydroxide in accordance with the scheme $Pb(OH)_2 \rightarrow PbO + H^{\cdot} + OH'$ whilst that of the red modification is due to the preliminary condensation of several simple molecules to the complex $2PbO,Pb(OH)_2$.

H. W.

The System Copper–Oxygen. E. MOLES and M. PAYÁ (*Anal. Fís. Quím.*, 1922, 20, 563—570).—The initial temperature of absorption of oxygen by copper is about 350°; at this temperature also the dissociation of cupric oxide begins. Copper oxide wire commonly used in analysis is a solid solution of cuprous oxide in cupric oxide. Powdered cupric oxide undergoes contraction on heating, and a decrease in dissociation pressure takes place. The change is superficial.

G. W. R.

Topochemical Reactions. Homologous and Substituted Forms of Production. V. KOHLSCHÜTTER and VL. SEDELINOVICH (*Z. Elektrochem.*, 1923, 29, 30—44; cf. this vol., ii, 133).—Specimens of electrolytic copper hydroxide have been examined with the object of ascertaining to what extent the form is maintained in which the hydroxide was produced when topochemical changes take place. Nine varieties of copper hydroxide were investigated and as topochemical changes leading directly to new substances the following reactions were examined. Spontaneous formation of oxide, conversion into sulphide by means of hydrogen sulphide, and the further conversion to cuprous sulphide, the action of hydrogen peroxide, which through a peroxide forms cupric oxide with the liberation of oxygen, the reduction to cuprous oxide with hydrazine, and the formation of basic salts by the action of concentrated solutions of potassium chloride. The various forms of copper oxide were identified by the velocity of the change into oxide, and by their behaviour as suspensions. The observation of the velocity of sedimentation served also for the investigation of the products of the reactions. It is shown that there is a definite connexion between the form of the initial material, the course of the reaction, and the form of the product. The form of the initial material is conditioned largely by the velocity of formation. The forms of a substance obtained by changing the determining conditions of a reaction constitute a *form-homologous series*, from which by means of topochemical reactions other form-homologous series may be produced. The members of these series correspond with those of the first in behaviour and form.

J. F. S.

Cuprous Compounds. J. ERRERA (*Bull. Acad. roy. Belg.*, 1921, [v], 7, 361—386).—The electrolysis of solutions of chlorine-free sodium hydrogen carbonate, using a copper anode, gives rise to the basic carbonate, $2CuCO_3,2Cu(OH)_2,H_2O$, which is superimposed upon a layer of cuprous oxide. Deville's salt, $Na_2CO_3,CuCO_3,3H_2O$, is probably an active complex in solution during electrolysis. The

change of anode potential was followed by means of a normal electrode, Hg|HgO|$NaHCO_3$ (46 g. per litre), for which the constant potential ($E_{H=0}$) is 0·433 volt at 15°.

The electrolysis of a solution of carbon dioxide (saturated at 20 atmospheres pressure), using a copper anode, results in the formation of a green carbonate. No azurite is formed. "Black copper," an unstable modification of the metal which rapidly passes into red copper, particularly in presence of acid, is deposited on the cathode.

The electrolysis of a solution of sodium silicate, using a copper anode, gives an insoluble silicate superimposed upon cuprous oxide. The formation of the latter was not prevented by using a water-cooled anode, and was therefore not due to secondary changes resulting from local heating.

The formation of cuprous salts by a reversible reaction occurring in solutions of cupric sulphate also occurs with cupric nitrate. The latter, in the presence of metallic copper, in the cold and under the influence of an electrical current, or at higher temperatures in the absence of a current, gives rise to a cuprous salt, oxidisable with potassium permanganate. For a *N*/5-solution at 97°, the concentration of cuprous ions is 5×10^{-4} g. per litre, and $[Cu^{\cdot\cdot}]/[Cu^{\cdot}]^2=5\times10^5$. Such solutions regenerate the oxide $2CuNO_3+H_2O \rightleftharpoons Cu_2O+2HNO_3$. A similar hydrolysis seems to occur when copper is in contact with the cupric salts of a weak acid, which may explain the formation of cuprous oxide on the anodes as described above.

When copper is left in contact with an aqueous suspension of its carbonate in a closed vessel in complete absence of air, etc., cuprous oxide is formed after a short time in the cold. (This points to the intermediate formation of cuprous salts, and may explain the occurrence of cuprite in minerals containing native copper and malachite.) Copper silicate and copper, under similar conditions, also give rise to small but appreciable quantities of cuprous oxide. E. E. T.

Surface Tension of Mercury in Contact with Oxygen. J. Palacios and E. Lasala (*Anal. Fís. Quím.*, 1922, **20**, 505—508; cf. A., 1921, ii, 304).—The surface tension of freshly-distilled mercury in contact with oxygen does not decrease and is practically the same as in a vacuum. In contact with air, however, the surface tension gradually decreases. G. W. R.

Separation of Mercury into Isotopes in a Steel Apparatus. William D. Harkins and S. L. Madorsky (*Nature*, 1923, **111**, 148).—An apparatus is figured and described by means of which long-continued and repeated fractional vaporisation from a steel trough in a vacuum at low pressures can be effected. It has thus been found possible to obtain a difference of 0·1 unit in the atomic weight of mercury. Cooling by ice was employed. A. A. E.

Dilatometric Study of the Alloys of Aluminium with Magnesium and Silicon. A. Portevin and P. Chevenard (*Compt. rend.*, 1923, **176**, 296—298).—The dilatometric curves

have been obtained for an alloy containing 0·95% of magnesium and 1·25% of silicon, the alloy having been originally annealed and then submitted to ten successive thermal cycles. The final temperature of each successive heating was increased until at the seventh heating the alloy commenced to melt. In curves three to six, at temperatures above 350°, there was a contraction of the alloy due to gradual solution of magnesium silicide, and on cooling precipitation of the silicide is marked by a progressive expansion, which is, however, retarded and incomplete, so that there is a residual contraction, which is greater the higher the temperature to which the alloy was heated. After these thermal cycles, therefore, there is, in increasing amount, an excess of silicide in solution, resulting in a more and more accentuated tempering effect.

The phenomenon of spontaneous return at the ordinary temperature can also be studied by means of a differential dilatometer, and curves are given for the above alloy. Experiments conducted between 20° and 80° show that the velocity of precipitation of the silicide increases according to an exponential law of the temperature and doubles for an interval of about 10°. W. G.

Hydrates and Hydrogels. I. Aluminium Hydroxide. RICHARD WILLSTÄTTER and HEINRICH KRAUT (*Ber.*, 1923, **56**, [*B*], 149—162).—During the application of aluminium hydroxide in the adsorption of enzymes, variations in activity are observed which do not appear to be simply related to the dispersivity of the hydrogel. The present investigation is concerned with the possibility that the varieties of aluminium hydroxide obtained by precipitation from the salts are different hydrates of aluminium oxide, and the relationship between the chemical properties of the varieties and their adsorptive capacity for enzymes.

Aluminium hydroxide has been obtained by four different methods, for the full details of which the original communication must be consulted. Variety *A* is prepared by precipitating aluminium sulphate solution with concentrated ammonia and protracted heating of the precipitate with ammonia; it is a pale yellow, plastic mass. Variety *B*, a very pale yellow, plastic, viscous mass, is obtained similarly to *A*, but the protracted heating is omitted. (An intermediate variety *b* is prepared by the dialysis of aluminium chloride with frequent addition of small quantities of ammonia against running water; it is related chemically to *B*, but in adsorptive capacity more closely resembles *A*.) Variety *C* is pure white in colour, voluminous, and very finely divided; it is obtained by precipitating aluminium sulphate solution with dilute ammonia without protracted heating. Variety *D*, which is pure white in colour and coarsely powdered, is obtained by passing a slow stream of carbon dioxide into a solution of potassium aluminate. The chemical behaviour of the different varieties towards sodium hydroxide (1%), warm acetic acid (12%), and hydrochloric acid (1%, 15%, and 35%) is described in detail. Variety *B* appears to be the most decidedly acidic, but loses this property to a considerable degree when subjected to protracted heating, owing to

conversion into *A*. Basic properties are most pronounced in *D*. The differences in behaviour cannot be explained on purely chemical or purely chemico-colloidal grounds. Different chemical types certainly exist, but their behaviour is as yet insufficiently elucidated.

The desiccation of the varieties when preserved in a desiccator over sulphuric acid has been studied; the process takes place very slowly. It is only possible to state that it is thus shown that the different gels contain a number of different chemical hydrates. The step-wise dehydration at gradually increasing temperatures has also been examined, and for this purpose a special form of apparatus is figured and described in the text. Definite steps in the dehydration appear to be indicated.

The adsorptive capacity of the different varieties for invertin and lipase has been examined. This appears to be affected to a very marked extent by the dilution of the solution. Invertin is accompanied by substances which greatly inhibit adsorption from concentrated solution, but have a much less pronounced action in dilute solution. A similar reaction is not shown by the companions of lipase. Invertin is only adsorbed to a slight extent by variety *D*, as would be expected from the physical properties of the micro-crystalline, coarse material. Whereas, however, *A* and *B* are very similar with regard to dispersivity, the latter, which is the more active chemically, is the more highly absorbent. The most surprising result is the high adsorptive capacity of *C*, which, in spite of its finely divided, non-plastic character, is superior to either *A* or *B*. A simple relationship does not exist between the colloidal properties of the aluminium hydroxides and their adsorptive capacities. Two different factors, the surface action and the differing chemical properties of the products, appear to be involved. These two factors, however, have not the same influence with all enzymes, since the relative activity of the aluminium hydroxide preparations towards invertin is not the same as towards lipase. H. W.

Cobalt Complexes. Werner's Formulæ and their Experimental Signification. P. Job (*Bull. Soc. chim.*, 1923, [iv], **33**, 6—21).—A lecture delivered before the Société Chimique de France. G. F. M.

The Catalytic Decomposition of Hexamminecobaltichloride. Robert Schwarz and Walter Krönig (*Ber.*, 1923, **56**, [*B*], 208—214).—In a previous communication, Schwarz and Bausch (A., 1921, ii, 404) have drawn the conclusion that the interaction of hexamminecobalti- and chloropentamminecobalti-chloride solutions on alkali silicates is accompanied by the displacement of the ammine groups by the silicate complex. This conclusion is now found to be due to an analytical error. The process only causes the formation of silicates and the silicato-compounds which have been described should be deleted from the literature. Slow decomposition of hexamminecobaltichloride solutions is caused by silicic acid gels, but the quantitative nature of the process is difficult to follow, and the change is more readily observed in the presence of

charcoal. The solutions are slowly decomposed in the presence of the latter at 20°, cobalt and ammonia being adsorbed, leaving a mixture of unchanged hexamminecobaltichloride and chloropentamminecobaltichloride in solution, which, however, is free from cobaltous salts. The reactions which occur may be represented by the equations: $[Co(NH_3)_6]Cl_3=[Co(NH_3)_5Cl]Cl_2+NH_3$; $[Co(NH_3)_6]^{+++}=Co^{+++}+6NH_3$; $[Co(NH_3)_6]Cl_3+3H_2O \longrightarrow Co(OH)_3+3NH_4Cl+3NH_3$. The change indicated by the second equation occurs readily also when aqueous solutions of the luteochloride are exposed to the light of a mercury lamp. Like the action of charcoal, it is inhibited by feeble acidity of the solution.

The maximum formation of the purpureochloride is observed in 1% solution; at higher concentrations, the ion, $[Co(NH_3)_6]^{+++}$, becomes more stable, whereas in more dilute solution reaction III preponderates. With an increased amount of carbon, the cobalt is completely adsorbed from a 0·5% solution of the luteochloride, and a solution of ammonia remains. With increasing concentration of the solution, the quantities of adsorbed cobalt diminish, whereas those of ammonia rapidly become constant. Contrary to the usual adsorptive process, the absolute amounts of adsorbed cobalt diminish with increasing concentration of the solution; the phenomenon is explained by the increased extent of the hydrolysis (equation III) in dilute solution. H. W.

Effect of Masked Anions on the Magnetic Susceptibility of Chromic and Chromyl Salts. B. Cabrera and S. Piña de Rubies (*Anal. Fis. Quim.*, 1922, **20**, 509—518; cf. A., 1922, ii, 612).—Solutions of chromic sulphate which when freshly prepared give no sulphate reaction undergo change on keeping, whereby electrical conductivity and sulphate reaction show a parallel increase. No appreciable variation in magnetic susceptibility, however, is observed. In the case of solutions of chromyl sulphate, on the other hand, an increase in magnetic susceptibility is observed. The change is supposed to consist of two successive unimolecular reactions, namely, $[(SO_4)_2Cr_2O] \longrightarrow SO_4[SO_4Cr_2O] \longrightarrow (SO_4)_2[Cr_2O]$. The quantitative aspect of these reactions is discussed.

G. W. R.

Determinations of the Density of Metals and Alloys at High Temperatures. III. The System Tin-Bismuth. K. Bornemann and Paul Siebe (*Z. Metallk.*, 1922, **14**, 329—334).—The specific volumes of tin, bismuth, and tin-bismuth alloys have been determined at temperatures up to 900°. In every case, the volume is directly proportional to the temperature. Tin expands 2·8% during melting, and bismuth contracts 3% (cf. *J.S.C.I.*, 1923, 229A). A. R. P.

The System Tin-Arsenic. Qasim Ali Mansuri (T., 1923, 123, 214—223).

Complex Compounds of Tin. Hydrolysis of Stannic Chloride and Chlorostannates. J. de la Puente (*Anal. Fis. Quim.*, 1922, **20**, 486—495).—Stannic chloride reacts with four mole-

cules of sodium hydroxide, giving a complex of the composition $[SnCl_2(OH)_4]Na_2$, which can also be obtained by the reaction of one molecule of orthostannic acid with two molecules of hydrochloric acid and sodium hydroxide. Potassium chlorostannate in 1% solution is completely dissociated into stannic chloride and potassium chloride. The dissociation is partly prevented by the presence of a large excess of potassium chloride. Attention is directed to the possibility of a series of complexes intermediate between chlorostannic acid, H_2SnCl_6, and the hydrated stannic acid, $H_2Sn(OH)_6$. G. W. R.

Preparation of Pure Zirconium Oxide. HERMANN VON SIEMENS and HERBERT ZANDER (*Wiss. Veröffentl. Siemens Konzern*, 1922, 2, 484—488; from *Chem. Zentr.*, 1923, i, 21).—A Brizilian zircon mineral containing ZrO_2 67·8%, SiO_2 22·2%, Fe_2O_3,TiO_2 8·7%, is mixed with 25% of carbon and treated with a stream of chlorine at 1000—1200°. From the mixture of chlorides thus formed, zirconium oxychloride is obtained by crystallisation from aqueous solution. Ignition of this in air yields zirconium oxide. G. W. R.

Purification and Analysis of Zirconium Dioxide. F. G. JACKSON and L. I. SHAW (*J. Amer. Chem. Soc.*, 1922, **44**, 2712—2714).—With the object of purifying zirconia for the investigation of this substance as a refractory, and particularly with the object of removing low melting impurities, the authors have investigated methods of purification. It is found that zirconia is best dissolved by fusion with a mixture of borax and sodium carbonate. The fusion, after treatment with dilute hydrochloric acid, cannot be separated from the insoluble residue by direct filtration. It is found that by precipitating the zirconium and other metals as hydroxides in the unfiltered solution the insoluble residue is entangled in the precipitate and may then be filtered and washed. The hydroxide can then be dissolved on the filter-paper by warm dilute hydrochloric acid and on repeatedly pouring the filtrate through the filter-paper a clear filtrate may be obtained. This contains all the iron, aluminium, and zirconium and most of the titanium present in the original material. The solution of chlorides is diluted, and treated with the calculated amount of sulphuric acid. A gelatinous precipitate of basic sulphates of zirconium and titanium is obtained, whilst the whole of the iron and aluminium, and some of the titanium and zirconium, remain in solution. The solution is heated, but not boiled, with constant stirring to coagulate the precipitate, which is filtered and washed until the washings give no reaction for iron with ammonium thiocyanate. This process, which is slow and tedious, is efficient for removing iron, aluminium, and silica, but does not remove much of the titanium. J. F. S.

Reaction of Methane and of Acetylene with Zirconium Tetrachloride. F. P. VENABLE and R. O. DEITZ (*J. Elisha Mitchell Sci. Soc.*, 1922, **38**, 74—75).—Zirconium tetrachloride

reacts with ammonia, phosphine, and hydrogen sulphide, forming compounds which, when heated, yield zirconium nitride, phosphide, and sulphide, respectively. Zirconia reacts with carbon at a high temperature, forming the carbide ZrC. The interaction of zirconium tetrachloride with methane gives rise to three distinct solid products, namely, black particles, light brown particles, and colourless masses with black inclusions. The first, which was present in small quantity, contained 32·09% C. The reaction with acetylene begins on gentle heating and is exothermic.

CHEMICAL ABSTRACTS.

Isolation of the Oxide of a New Element. ALEXANDER SCOTT (T., 1923, **123**, 311—312).

The New Element Hafnium. D. COSTER and G. HEVESY (*Nature*, 1923, **111**, 182; cf. this vol., ii, 80).—In order more accurately to estimate the amount of hafnium in the samples examined, a known quantity of tantalum (73) was added and the intensities of the lines were compared. A large number of zirconium minerals have been examined, and all have been found to contain between 5 and 10% of hafnium. Moreover, a chemical method of separation (details of which are not given in the present brief communication) has resulted in the production, on the one hand, of a substance containing about 50% of hafnium, and, on the other, of zirconium which did not yield any hafnium lines.

A. A. E.

The Element of Atomic Number 72. G. URBAIN (*Compt. rend.*, 1923, **176**, 469—470); G. URBAIN and A. DAUVILLIER (*Nature*, 1923, **111**, 218; cf. this vol., ii, 80, and preceding abstract).—The lines observed in the high-frequency spectra of zirconium minerals by Coster and Hevesy appear to be identical with those previously observed in the case of ytterbia by Urbain (A., 1911, ii, 115; see also A., 1922, ii, 505, and Dauvillier, A., 1922, ii, 463). Priority is therefore claimed for the name "celtium," then given to the element producing the lines in question, as against "hafnium." It is, however, admitted that to celtium was incorrectly ascribed properties intermediate between those of lutecium and scandium. Moreover, other cases are quoted in support of the contention that it is not impossible for a quadrivalent element, such as that under consideration, to be present in the mother-liquors after fractionation of the rare earths. A. A. E.

The New Element Hafnium. D. COSTER and G. HEVESY (*Nature*, 1923, **111**, 252).—A reply to Urbain and Dauvillier (preceding abstract).—Hafnium is considered to differ from celtium in that there is no difficulty in separating the former from contents of rare earths, nor does it appear to yield the characteristic optical spectrum ascribed by Urbain to celtium. It is maintained that the *X*-ray spectrum of hafnium is not coincident with that described by Dauvillier. The hafnium content of the earth's crust is estimated to be more than 1 part per 100,000. A. A. E.

Germanium. IV. Germanium Tetraiodide. L. M. DENNIS and F. E. HANCE (*J. Amer. Chem. Soc.*, 1922, **44**, 2854—2860; cf. A., 1922, ii, 150, 302).—Germanium tetraiodide is prepared by passing iodine vapour in a current of carbon dioxide over crystalline germanium heated at 250—360°. The tetraiodide sublimes and a deposit of yellow and red crystals and a red liquid are formed in the cooler parts of the tube. Between the boat containing the germanium and the red iodide a small deposit of yellow crystals formed; these are germanous iodide, GeI_2, which crystallises in the hexagonal system with angles of 120°. Germanium tetraiodide at the ordinary temperature is of the colour of coral when in lump form; when powdered, it has an orange colour. The colour depends on the temperature, at −185° it is canary-yellow; −50°, buff; −10°, orange; +35°, salmon; +50°, brick-red; +90°, red, and +144°, ruby red. It melts sharply at 144° to a ruby-coloured liquid. It forms regular octahedra and has $d_{26^\circ}^{26^\circ}$ 4·3215. Concentrated sulphuric acid has no action on it, and since all other liquids examined either dissolve or decompose it, the density was determined by means of sulphuric acid. Germanium tetraiodide sublimes at temperatures just above the melting point without dissociation, but at 440° dissociation occurs according to the equation $GeI_4 \rightleftharpoons GeI_2+I_2$. It is practically unchanged when exposed to air for five months, but is decomposed by a small quantity of water, giving germanium dioxide. Cold concentrated sulphuric acid produces no change in it in twenty-four hours, but on heating at 80° there is a slow liberation of iodine. It is slowly dissolved by cold 1 : 4-potassium hydroxide, concentrated nitric acid turns it black with liberation of nitrogen dioxide, and concentrated hydrochloric acid dissolves it very slowly. Concentrated ammonia solution decomposes it to form a white solid which is soluble in water, whilst dry gaseous ammonia slowly converts it into a white powder which is soluble in water. Germanium tetraiodide dissolves in the following solvents, giving solutions of the colours named; in all cases the solutions were quite unchanged after keeping for four months: benzene, reddish-orange; carbon disulphide, reddish-orange; methyl alcohol, deep orange; ethylene dichloride, light orange; chlorobenzene, reddish-orange; carbon tetrachloride, light orange; ethylene glycol, light yellow, and ethylene chlorohydrin, light yellow. It is also dissolved by the following solvents, giving solutions varying in colour from deep orange to pale yellow, but in every case a slow decomposition takes place: hexane, amyl alcohol, chloroform, nitrobenzene, light petroleum, butanol, and acetic acid. Many solvents decompose it at once. J. F. S.

Measurements of the Density of Metals and Alloys at High Temperatures. IV. The Systems Antimony-Zinc and Aluminium-Antimony and the Metals Silver and Magnesium. F. SAUERWALD (*Z. Metallk.*, 1922, **14**, 457—461).—The specific volumes of zinc-antimony alloys are greater than the values calculated from those of the two metals, both at

ordinary and at elevated temperatures, and a maximum value is obtained at a composition corresponding with Zn_3Sb_2. Aluminium-antimony alloys show deviations from the calculated values only at the ordinary temperature, an abrupt change occurring at the composition corresponding with AlSb. At 1000°, this compound is decomposed and the specific volume of any alloy may then be calculated from those of its constituents. The specific volumes of silver at temperatures up to 1100° and of magnesium at 780° have been determined [cf. *J.S.C.I.*, 1923, 229A]. A. R. P.

Examination of the Alleged Antimonious Hydroxides. Charles Lea and John Kerfoot Wood (T., 1923, **123**, 259—265).

The Crystal Structure of Bismuth. L. W. McKeehan (*J. Franklin Inst.*, 1922, **195**, 59—66).—New data have been obtained using the powder method and the *X*-rays of molybdenum. The results are best explained by means of a simple rhombohedral space lattice, with a set of rhombohedral axes, mutually inclined at 57° 16′. From the absence of any planes attributable to (422)′, (330)′, and (411)′, it is deduced that the bismuth atoms are not uniformly placed along the trigonal axis. The distances between adjacent atom centres have been calculated, and are shown in a diagram. W. E. G.

The Anode Oxidation of Gold. III. Fr. Jirsa and Ot. Buryánek (*Chem. Listy*, 1922, **16**, 328—330; cf. A., 1922, ii, 713, this vol., ii, 80).—It is concluded that the oxidation of gold anodes in dilute sulphuric acid takes place in four stages. The first, which requires the least *E.M.F.*, is the solution of gold in sulphuric acid, to form aurous sulphate. This is hydrolysed in the second stage to auric hydroxide, $2Au_2SO_4+2H_2O \longrightarrow 2Au(OH)SO_4+H_2SO_4+2Au$; $Au(OH)SO_4 \longrightarrow Au(OH)_3+H_2SO_4$. In the third stage, the gold again dissolves in the acid, this time forming auric sulphate, which also undergoes hydrolysis in dilute solution, going first into the basic sulphate and then into auric hydroxide, as before. In the fourth stage, the tervalent gold becomes quadrivalent, forming AuO_2. Since at the ordinary temperature the dissociation pressure of this oxide is above one atmosphere, it decomposes, liberating oxygen and forming auric oxide. The four stages may be thus shown: I. $Au \longrightarrow Au^{\cdot}$; II. $3Au^{\cdot} \longrightarrow Au^{\cdot\cdot\cdot}+2Au$; III. $Au \longrightarrow Au^{\cdot\cdot\cdot}$; IV. $Au^{\cdot\cdot\cdot} \longrightarrow Au^{\cdot\cdot\cdot\cdot} \longrightarrow Au^{\cdot\cdot\cdot}$.

The hydrolysis of the aurous sulphate explains why oxidation to bivalent gold does not take place. It is found, generally, that a gold anode in dilute sulphuric acid exhibits typical passivity, and that oxidation to auric oxide proceeds without the formation to any appreciable extent of intermediate products. The speed with which gold anodes, in the presence of lower degrees of oxidation, become passive is so great that it is impossible to isolate any intermediate oxidation product. The solubility of auric hydroxide increases with the concentration of the acid, whilst the passivity of a rotating gold anode decreases. Since with a stationary

anode the final passivity in concentrated acid is greater than in dilute, it is only possible to show the existence of the intermediate stages $Au^{\cdot}$ and $Au^{\cdot\cdot\cdot}$ if a rotating anode is used. The existence of auric dioxide (AuO_2) is proved beyond doubt by the discharge curve and the depolarisation curve given in the original. R. T.

Mineralogical Chemistry.

Parsonsite, a New Radioactive Mineral. ALFRED SCHOEP (*Compt. rend.*, 1923, **176**, 171—173).—The green colour of some specimens of torbernite from Kasolo, Katanga, Belgian Congo (A., 1922, ii, 155), is obscured by a brown powder. This is readily separated by washing in water, and consists of minute crystals (monoclinic or triclinic) with d^{17} 6·23, $n>1·99$. When heated, it turns yellow and fuses to a black bead; it is readily soluble in acids. Analysis gave:

PbO.	CuO.	UO_3.	P_2O_5.	TeO_3.	MoO_3.	CaO.
44·71	0·25	29·67	15·08	3·01	0·43	0·63

Al_2O_3.	CO_2.	Insol.	H_2O.	Total.
1·23	1·19	1·51	1·56	99·47

Deducting impurities (copper due to admixed torbernite) the formula is $2PbO,UO_3,P_2O_5,H_2O$. Tellurium and molybdenum were detected also in the torbernite; and the pitchblende from Kasolo contains selenium and molybdenum. L. J. S.

Presence of the Element No. 72 (Hafnium) in Malacon and Alvite. V. M. GOLDSCHMIDT and L. THOMASSEN (*Norsk Geologisk Tidsskrift*, 1923, **7**, 61—68).—The relation of element 72 to zirconium suggested the examination of some anomalous zircon-like minerals by the method of *X*-ray spectrum analysis (A. Hadding, A., 1922, ii, 780, 855), using a rock-salt crystal turned by clockwork. Malacon from Hitterö, Norway, showed the lines of zirconium, element 72, iron, manganese, yttrium, and trace of tungsten. Alvite from Kragerö, Norway, showed the lines of zirconium, strong 72, iron, manganese, aldebaranium, yttrium, weak thorium, and perhaps traces of cerium and tungsten. The formula of alvite is written as $(Zr,72,Th)O_2,SiO_2$. L. J. S.

Meteoric Iron from Glasgow, Kentucky. GEORGE P. MERRILL (*Amer. J. Sci.*, 1923, [v], **5**, 63—64; *Chem. News*, 1923, **126**, 63—64).—Two much-oxidised masses weighing about 25 and 20 lb. were recently ploughed up. The structure is that of a coarse octahedrite. Analysis by J. E. WHITFIELD gave:

Fe.	Ni.	Co.	S.	P.	C.	Cl.
70·63	7·27	0·62	0·11	0·12	0·06	0·36

Fe,Ni oxides.	SiO_2.	Ign.	Total.
19·22	trace	1·65	100·04

The percentage of chlorine corresponds with 0·62% of lawrencite ($FeCl_2$). This is high and accounts for the ready disintegration of the material which is difficult to arrest. L. J. S.

Meteoric Iron from Somerset County, Pennsylvania. George P. Merrill (*Amer. J. Sci.*, 1923, [v], 5, 175—176).—An oxidised mass of about 18 kg. was ploughed up in 1922 on Allegheny Mountain, and is called the New Baltimore iron. It is an irregularly granular mass, readily breaking into fragments; and it therefore probably belongs to the same fall as the Mt. Joy iron found 90 miles away. Analysis by J. E. Whitfield gave:

Fe.	Ni.	Co.	P.	Si.	C.	Total.
93·256	6·420	0·325	0·037	0·010	0·015	100·063

Copper, manganese, and sulphur are absent. L. J. S.

Analytical Chemistry.

New Vessel for Electrometric Titration. W. T. Bovie (*J. Amer. Chem. Soc.*, 1922, 44, 2892—2893).—A new form of glass vessel for use in electrometric titrations is described. The vessel has a capacity of about 150 c.c.; it is oviform in shape and at its wider end is fitted with four tubulures, one in the exact centre being for the burette jet and the other three situated at equidistant points on a circle being for the hydrogen electrode, calomel electrode and hydrogen inlet, respectively. The vessel is attached to a stout glass rod at its lowest point which slips into a hole in a heavy support. J. F. S.

Some Applications of Oxygen Electrode, Air Electrode, and Oxidation Potential Measurements to Acidimetry and Alkalimetry. N. Howell Furman (*J. Amer. Chem. Soc.*, 1922, 44, 2685—2697).—An oxygen or air electrode, constructed in the manner generally adopted for a hydrogen electrode, may be used for the titration of the acid or alkali in the presence of oxidising agents such as potassium dichromate or potassium permanganate. The method yields accurate results, and by using an empirical scale the *E.M.F.* readings of the cells are built up as indicated. Platinised platinum|oxygen||acid or alkaline solution of an oxidising agent| calomel-electrode; will serve to give a quantitative indication of the hydrogen-ion concentration. J. F. S.

Mixtures of Tartrates and Phosphates as Buffers. Antagonistic Action of Calcium Chloride. L. J. Simon and L. Zivy (*Compt. rend.*, 1923, 176, 136—138; cf. A., 1922, ii, 880).—The addition of calcium chloride exerts inverse effects in the neutralisation of tartaric acid and phosphoric acid. In the case of tartaric acid, the neutral zone, as between helianthin and phenolphthalein

as indicators, tends to disappear, whilst in the case of phosphoric acid it is doubled. This phenomenon is additive, and if the two acids are mixed in equimolecular proportions the neutral zone and the correlative buffer effect are invariable. W. G.

Method for the Micro-estimation of Chlorine in Blood. PAUL IVERSEN and M. J. SCHIERBECK (*Ugeskr. laeger*, **84**, 454—456; from *Chem. Zentr.*, 1922, iv, 1076).—0·1 C.c. of blood is added to 0·8 c.c. of 0·1*N*-sodium hydroxide and 4 c.c. of 0·45% zinc sulphate solution. After heating for three minutes, the liquid is filtered and treated with 0·2 c.c. of 29% nitric acid and 1 c.c. of 0·01*N*-silver nitrate solution. When the precipitate has settled, the clear supernatant liquid is titrated with 0·005*N*-ammonium thiocyanate in the presence of one drop of saturated iron ammonium alum solution. G. W. R.

Bang's Method for the Micro-estimation of Chlorine. PAUL IVERSEN (*Ugeskr. laeger*, **84**, 456—458; from *Chem. Zentr.*, 1922, iv, 1076).—Discordant results in the micro-estimation of chlorine are attributed to variations in the amount of ethyl alcohol used for the extraction of blood and in the method of extraction. G. W. R.

The Reaction between Hypochlorite and Potassium Iodide. I. M. KOLTHOFF (*Rec. trav. chim.*, 1922, **41**, 615—626; cf. following abstract).—Hypochlorous acid to which a solution of sodium hydrogen carbonate has been added reacts with potassium iodide according to the equation $3HClO+I' \longrightarrow IO'_3+3H^{\cdot}+3Cl'$, the formation of hypoiodite being a preliminary stage in the oxidation of the iodine. When the quantities of each substance are equivalent, the hypoiodite reacts with iodide, liberating iodine. The rate of transformation of hypoiodite into iodate depends on the hydrogen-ion concentration of the solution. In the presence of mineral acids, the end-point cannot be ascertained by means of starch, as no iodine-ions remain in the solution; moreover, iodate may be transformed into chloro-compounds of iodine in solutions containing sulphuric or hydrochloric acid. It is stated that Klimenko's method of estimation of hypochlorite and chlorine in presence of each other (A., 1904, ii, 205) is untrustworthy. Chlorine in sodium hydrogen carbonate solution may be titrated in a similar manner to iodine. H. J. E.

The Titration of Hypochlorite. I. M. KOLTHOFF (*Rec. trav. chim.*, 1922, **41**, 740—750).—Solutions of hypochlorites on being kept are transformed into chloride, chlorate, and also into chlorite. In estimating hypochlorite in bleaching powder by means of potassium iodide in sulphuric acid solution, the presence of chlorite introduces an error, as it reacts according to the equation $ClO_2'+4I'+4H^{\cdot} \longrightarrow 2I_2+Cl'+H_2O$, although chlorates have no such influence. Chlorite reacts very slowly, if at all, with arsenious acid or with potassium iodide in sodium hydrogen carbonate solution, so that the titration of hypochlorite may be carried out accurately with either of these reagents according to Treadwell's

method. In effecting the titration by Pontius's method, the operation must be carried out slowly in presence of a large excess of sodium bicarbonate (cf. *J.S.C.I.*, 1923, 181A). H. J. E.

Detection of Hypochlorites and Chloroamines in Milk and Cream. PHILIP RUPP (*U.S. Dept. Agr. Bull.*, 1922, **1114**, 1—5).—Five c.c. of the milk or cream, 1·5 c.c. of a 7% solution of potassium iodide, and 4 c.c. of hydrochloric acid (1 : 2) are heated in a water-bath at 85° for ten minutes, cooled, and 0·5 to 1 c.c. of starch solution is added. The presence of available chlorine in amounts as low as 1 in 50,000 is indicated by the pale yellow colour of the milk below the curd changing to a light reddish-purple, passing through reddish-purple to a deep bluish-purple as the amount of chlorine is increased. Milk pasteurised, after the addition of hypochlorites, at 63° for thirty minutes reacts in the same way as raw milk. CHEMICAL ABSTRACTS.

Analytical Investigation of Chlorates. P. POCH (*Anal. Fis. Quim.*, 1922, **20**, 662—666).—The reactions for chlorates are discussed. Potassium chlorate and ammonium thiocyanate heated together at 140—150° produce an orange-red mass with deflagration. The mass contains carbon, nitrogen, and sulphur, and when heated on platinum foil burns with a violet flame, leaving a small residue of carbon. The orange-red colour may be used as a test for chlorates by adding 1 c.c. of 0·5*N*-ammonium thiocyanate to 1 c.c. of a solution of a chlorate and evaporating to dryness. The orange-red coloration is given even with 0·00025 g. of potassium chlorate. G. W. R.

A Method for the Simultaneous Estimation of Sulphur and Halogen in Organic Compounds. CLIFFORD S. LEONARD (*J. Amer. Chem. Soc.*, 1923, **45**, 255—257).—A detailed account of Klason's method for the combined estimation of sulphur and halogens in an organic substance (A., 1886, 918). The material to be analysed is placed in a porcelain boat at one end of a combustion tube which contains in sequence a platinum spiral, a boat filled with fuming nitric acid, and a second platinum spiral. The first end of the tube has attached to it a bubbling flask of fuming nitric acid, and the other end is drawn out so as to dip into water or silver nitrate solution. The combustion is thus carried out in an atmosphere of nitrous fumes, and air or oxygen may be slowly passed through the tube. At the end of the combustion, the tube and its contents are rinsed with distilled water, the rinsings being added to the liquid in the receiving flask. In this liquid, the halogens and sulphur may then be estimated as is done after a Carius combustion. W. G.

Micro-estimation of Sulphuric Acid and Sulphur in Organic Substances by the Benzidine Method. G. ZIMMERLUND and O. SVANBERG (*Svensk. Kem. Tidskr.*, 1922, **34**, 139—146; from *Chem. Zentr.*, 1922, iv, 1094).—The solution containing sulphuric acid is exactly neutralised and precipitated with a solution of benzidine hydrochloride. The precipitate is centrifuged

and the total filtrate titrated with 0·05*N*-sodium hydroxide and phenolphthalein according to Bang's method (*Mikrobestimmung von Blutbestandteilen*, 1922). The sulphuric acid content is derived from the difference between the titre thus obtained and the titre of the acid benzidine solution. Directions are given for the preparation of the benzidine hydrochloride solution. G. W. R.

Volumetric Estimation of Sulphates in Sea-water. José Giral Pereira (*Anal. Fís. Quím.*, 1922, **20**, 577—585).—The method consists in boiling the solution containing an alkali sulphate with excess of a solution of barium chromate in 0·1*N*-hydrochloric acid. Excess of calcium carbonate is added and after filtering, 5 c.c. of fuming hydrochloric acid are added for each 100 c.c. of filtrate, followed by excess of solid potassium iodide. By the action on the alkali chromate (equivalent to the original sulphate), iodine is liberated and may be titrated in the usual way with thiosulphate. G. W. R.

Refractive Indices of Selenic and Selenious Acid. Hosmer W. Stone (*J. Amer. Chem. Soc.*, 1923, **45**, 29—36).—The refractive indices of solutions of selenic and selenious acid in water have been determined for concentrations varying between 0·00% and 98·98% for selenic acid and 0·00% and 79·14% for selenious acid, using an Abbé refractometer and sodium light at 20°. Tables have been constructed giving the refractive indices of solutions of the two acids for every percentage value over the whole range measured. Using this method, the two acids may be rapidly and accurately estimated in solution. Selenic acid may be estimated gravimetrically as follows. The sample, 0·2—0·5 g., is treated with 50 c.c. of concentrated hydrochloric acid and diluted to 75—100 c.c. with water. The solution is heated to boiling and 30 c.c. of saturated aqueous sulphur dioxide solution are added. The solution is maintained at 90° until the red precipitate first formed turns black and further additions of sulphur dioxide gave no red precipitate. After the reaction mixture had been kept four to five hours at 80—90°, the precipitate was collected on a Gooch crucible, and dried at 105—110°. J. F. S.

Estimation of Nitric Oxide. A. Koehler and M. Marqueyrol (*Mém. Poudres*, 1922, **19**, 359—361).—Excess of oxygen is added to the gaseous mixture in the presence of a liquid secondary amine, such as ethylaniline, which absorbs the nitrous anhydride formed. The excess of oxygen is removed with alkaline pyrogallol and the contraction of volume gives the volume of nitric oxide. Under atmospheric pressure, ethylaniline dissolves its own volume of carbon dioxide, so that if this gas is present considerable excess of oxygen should be added so as to keep the partial pressure of the carbon dioxide low. A high degree of accuracy is attainable. H. C. R.

Detection of Nitrites in Water. Rodillon (*J. Pharm. Chim.*, 1923, [vii], **27**, 64—65).—The author concedes priority to Denigès

(*Bull. Sci. Pharmacol*, 1914) for the use of resorcinol in sulphuric acid solution as a reagent for nitrites. G. F. M.

The Detection of Nitric Acid by Ferrous Sulphate. CARL FAURHOLT (*Ber.*, 1923, **56**, [*B*], 337—341).—The customary brown-ring test for nitric acid occasionally gives very erratic results. These are traced to insufficient rapidity in the reduction of nitric acid. The defect can be most readily remedied by the addition of hydrochloric acid, a drop of which (4*N*) is introduced previously to the addition of sulphuric acid. The brown coloration is produced immediately. The presence of 0·5 mg. of potassium nitrate in 2 c.c. of solution can be detected with certainty. The limit of applicability of the method lies at about 0·2 mg. if control solutions are used to obviate the disturbance caused by the formation of yellow solutions of ferric chloride.

The oxidation of ferrous sulphate in solutions containing nitric and hydrochloric acids appears to proceed in such a manner that the acids first react with one another and that the chlorine and nitrosyl chloride thus produced convert the ferrous into the ferric salt. The oxidation of ferrous sulphate by nitric acid which occurs at high concentrations of nitric and sulphuric acids or at elevated temperature in the absence of hydrochloric acid does not occur to an appreciable extent under the experimental conditions.

H. W.

Estimation of Nitrogen in Nitrates, Cellulose Nitrates, and Glyceryl Nitrates by Devarda's Method. A. KOEHLER, M. MARQUEYROL, and P. JOVINET (*Mém. des Poudres*, 1922, **19**, 348—350; 351—355; 356—358).—If any ammonia is present, it is estimated by distilling into acid in the usual way. The contents of the flask are then cooled and a volume of water is added equal to that which has been distilled over. Twenty-five g. of finely pulverised Devarda's alloy (Al=45%, Cu=50%, Zn=5%) are added and the flask is connected to a Kjeldahl distillation apparatus and hydrogen allowed to come off for fifteen to twenty minutes, after which it is gently boiled for ten minutes, and the ammonia formed is distilled into acid and estimated in the usual way, methyl-red being used as indicator. A blank determination must be carried out with the reagents used. In the case of cellulose nitrate, the ester is first hydrolysed with aqueous potassium hydroxide and hydrogen peroxide. The temperature must not exceed 60° until all the cellulose nitrate is dissolved, but the liquid is afterwards boiled until oxygen ceases to be given off and then cooled to the ordinary temperature. The nitrate is then reduced with Devarda's alloy as described above. The method can be applied to glyceryl nitrate, but to obtain accurate results the hydrolysis must be carried out below 40°. This is only possible with the aid of violent agitation. A form of glass agitator suitable for use in a conical flask for this purpose is illustrated. It is provided with two bulbs blown on the stem so as nearly to close up the mouth of the flask, and so prevent loss of the contents through splashing. After

forty minutes' treatment, the glyceryl nitrate is completely dissolved and the temperature increased to 70° for a few moments. The estimation is then carried out as described above. This method gives more accurate results than the nitron method.

H. C. R.

Separation of Arsenic from other Elements. N. TARUGI (*Gazzetta*, 1922, 52, ii, 323—332).—The quantitative separation of arsenic from antimony, tin, copper, lead, mercury, and iron may be effected as follows: the arsenate solution is heated for thirty minutes with hydrazine sulphate and sufficient sodium hydroxide to correspond with about one-half of the hydrazine. The liquid is then cooled and distilled for one and a half hours with concentrated hydrochloric acid, the distillate, which is found to contain the whole of the arsenic, being collected in a flask connected with a Péligot tube. The arsenic may then be estimated, either gravimetrically as sulphide, or after the distillate has been rendered alkaline to methyl-orange by means of sodium hydroxide, and then treated with excess of solid sodium hydrogen carbonate, by titration with iodine solution. T. H. P.

[Estimation of] Silicon in Aluminium. R. GUERIN (*Ann. Chim. Analyt.*, 1923, 5, 4—8).—The official French method for estimating iron, silicon, and aluminium oxide in metallic aluminium is described and the composition and nature of silicon-aluminium alloys are discussed. A method is also given for the estimation of combined silicon (as aluminium silicide) and of graphitoidal silicon in the alloys depending on the insolubility of the latter form in aqua regia and its solubility in a mixture of hydrofluoric and nitric acids (cf. *J.S.C.I.*, 1923, 186A). A. R. P.

Use of Malic, Maleic, and Fumaric Acids in Volumetric Analysis. N. A. LANGE and HARRY KLINE (*J. Amer. Chem. Soc.*, 1922, 44, 2709—2711).—The suitability of malic, maleic, and fumaric acids for use as standards in the titration of alkalis and potassium permanganate has been investigated. It is shown that the three acids, suitably purified, give accurate and trustworthy results when used to standardise sodium hydroxide or potassium hydroxide. The commercial products must, however, always be purified before use for the above-named purpose. In the case of maleic acid, the purification is effected by a single crystallisation from water containing four drops of nitric acid for every 200 c.c. of solution; after air drying, the crystals are dried to constant weight over sulphuric acid or in an oven at 90°. Phenolphthalein is the best indicator for this acid. Fumaric acid is purified and used in the same way as maleic acid, but in this case, owing to the smaller solubility of the acid, the titration must be effected at a higher temperature. Malic acid is purified by dissolving in hot acetone, filtering, adding carbon tetrachloride to the hot solution, and allowing to crystallise. The crystals are air-dried for twenty-four hours, then for an equal time over sulphuric acid or for two hours at 90—120°. Although maleic and fumaric acids

may be used as standards for potassium permanganate solutions, they are neither as accurate nor as convenient as sodium oxalate for this purpose. Succinic, malic, maleic, and fumaric acids cannot be used as standards for ammonium hydroxide solutions, and the two last-named acids cannot be used for iodine titrations.

J. F. S.

The Estimation of Potassium as Alum. (MLLE) DE LE PAULLE (*Compt. rend.*, 1923, **176**, 105—107).—The method is for use in estimating small quantities of potassium in rocks. It is based on the comparative insolubility of potash alum in 30% (by volume) aqueous ethyl alcohol. In alcohol of such a strength aluminium sulphate is readily soluble. The mineral is digested with sulphuric and hydrofluoric acids; the solution is evaporated to dryness, and the residue ignited at a dull red heat. A weighed portion of the residual sulphates is dissolved in water and the solution cooled, and sufficient alcohol is added to bring it to 30%. After the whole of the potash alum has separated, it is collected, washed with the dilute alcohol, dried, and weighed. W. G.

Estimation of Potassium Salts with Sodium Cobaltinitrite. E. CLERFEYT (*Bull. Soc. chim. Belg.*, 1922, **31**, 417—420).—The perchlorate method of estimating potassium salts is said to be unsatisfactory, but it is claimed that accurate results are obtained by the use of sodium cobaltinitrite, numerous analyses showing an agreement within 0·1 to 0·2% of the results obtained by precipitation with platinic chloride. The reagent is made up in two solutions: I. 28·6 g. of cobalt nitrate and 50 c.c. of glacial acetic acid are made up to 500 c.c. with water. II. A solution of 180 g. of sodium nitrite in 500 c.c. of water. The two solutions should be kept separately, and for use I is slowly added to II twenty-four hours before the estimation to permit of the precipitation within that period of any potassium in the technical sodium nitrite, in which case the solution must be filtered before use. An excess of the reagent is added gradually with mechanical stirring to as concentrated as possible a solution of the potassium salt, slightly acidified with acetic acid. Forty c.c. are required for 0·25 g. of potassium chloride in 25 c.c. of solution, and in any case not less than 10 c.c. of reagent are used. Stirring is continued for half an hour, and the beaker set aside until next day, when its contents are filtered on a tared filter, the precipitate washed with 10% acetic acid until the washings are colourless, and then once with 95% alcohol, and dried at 120°. The dried precipitate has the formula $K_2NaCo(NO_2)_6,H_2O$, and contains 20·74% K_2O. P. M.

Estimation of Potassium by Przibylla's Sodium Hydrogen Tartrate Method and its Application to the Analysis of Potassium Salts of the Alsatian Basin. PAUL HUBERT (*Ann. Chim. Analyt.*, 1923, **5**, 9—14).—The method of Przibylla (*Kali*, 1908, No. 18) as modified by Bokemuller (*ibid.*, 1918, No. 15) has been further modified and adapted to the estimation of potassium in Alsatian sylvinites of very varying richness. The method

consists essentially in adding a slight excess of sodium hydrogen tartrate to the solution containing a definite weight of the sample, filtering an aliquot part of the liquid, and titrating with sodium hydroxide free from carbonate. According to the richness of the sample, the quantities of reagents used are altered so that the percentage of potassium can be calculated directly from the amount of sodium hydroxide used (cf. *J.S.C.I.*, 1923, 181A). A. R. P.

Separation and Estimation of Sodium and Lithium by Precipitation from Alcoholic Perchlorate Solution. H. H. Willard and G. Frederick Smith (*J. Amer. Chem. Soc.*, 1922, **44**, 2816—2824).—A method for the quantitative separation of sodium and lithium is described. The method depends on the precipitation of sodium chloride from a mixture of the perchlorates by means of a butyl alcohol solution of hydrogen chloride, and is carried out as follows. The mixture of sodium and lithium salts must be converted into chlorides by any suitable method and must contain no trace of sulphate. The mixed chlorides are evaporated to dryness with an excess of perchloric acid. If potassium is present it is first separated by the usual perchlorate separation, and the filtrate after the addition of water is evaporated to dryness. The mixed perchlorates of sodium and lithium free from perchloric acid are dissolved in *n*-butyl alcohol, using at least 18·5 c.c. for each 0·1 g. of sodium chloride likely to be formed later. The mixture dissolves readily if the alcohol is boiled. Then 0·1 c.c. of 70% perchloric acid is added and the solution cooled to −15°, and 1·0—1·5 c.c. of 20% hydrogen chloride in *n*-butyl alcohol are added slowly from a burette with continuous stirring, after which sufficient of the hydrogen chloride solution is rapidly added to form a 6% solution. The solution is then heated to boiling for a few minutes, allowed to cool, and the sodium chloride filtered on a Gooch crucible, washed eight to ten times with a 6—7% solution of hydrogen chloride in *n*-butyl alcohol, dried for one hour at 250°, and ignited at 600° for five to eight minutes in a muffle furnace, cooled, and weighed. A correction of 0·6 mg. must be made for the sodium chloride remaining in each hundred c.c. of filtrate. The filtrate and washings, diluted with one-third of their volume of water, are evaporated to dryness. If the residue is brown, it must be heated on a gauze until fumes of perchloric acid are evolved, and if insufficient of this acid is present to effect the complete oxidation of the organic matter a little should be added. The colourless residue is treated with 0·5 c.c. of concentrated sulphuric acid and heated until the whole of the acid has been expelled. The beaker is cooled, 5—10 c.c. of water are added, and the lithium sulphate is transferred to a platinum crucible, evaporated to dryness, ignited to drive off all free acid, and finally heated at 600° in a muffle furnace for five to ten minutes. A correction of 0·7 mg. per 100 c.c. of filtrate and washings should be subtracted from the weight of lithium sulphate. The results given by the procedure are uniformly good. The solubilities of sodium perchlorate, lithium perchlorate, sodium chloride, and lithium chloride in

n-butyl alcohol at 25° have been determined along with the densities of the saturated solutions, and the following values are recorded: lithium perchlorate, 44·23; $d_4^{25}=1·1341$; sodium perchlorate, 1·83; $d_4^{25}=0·8167$; lithium chloride, 11·49; $d_4^{25}=0·8713$; sodium chloride, 0·014; $d_4^{25}=0·8060$. The solubilities are given in g. per 100 g. of solution. The densities, d_4^{25}, of solutions of hydrogen chloride in *n*-butyl alcohol have also been determined and the following recorded: 0%, 0·8060; 1%, 0·8130; 2%, 0·8195; 3%, 0·8255; 4%, 0·8315; 5%, 0·8370; 6%, 0·8425; 7%, 0·8485; 8%, 0·8540; 9%, 0·8590; 10%, 0·8635; 11%, 0·8685; 12%, 0·8730; 13%, 0·8770; 14%, 0·8810; 15%, 0·8850; 16%, 0·8895; 17%, 0·8935; 18%, 0·8960; 19%, 0·9010, and 20%, 0·9050. J. F. S.

Oxidimetric Estimation of Calcium, and its Employment in Technical Work. J. GROSSFELD (*Chem. Weekblad,* 1923, **20**, 39—41).—In the method of estimating calcium by adding excess of ammonium oxalate, filtering, and titrating an aliquot part of the filtrate with permanganate, the solution should contain a considerable quantity of a weak acid; phosphoric acid is most suitable, but the amount used must be carefully regulated. The procedure of Vürtheim and van Bers (A., 1922, ii, 869) is tedious, requiring two hours' heating on the water-bath. A simplified method, which may be carried out in a beaker, consists in dissolving the substance (containing not more than 0·140 g. CaO) in the cold in 20 c.c. 4*N*-phosphoric acid, adding with stirring exactly 20 c.c. of the oxalate solution (20 g. per litre), and finally 30 c.c. of 2·5*N*-sodium hydroxide; the solution is filtered through a fine-pored filter, and 50 c.c. are titrated with *N*/10-permanganate.

The method can be employed for fertilisers, foodstuffs, waters, and for estimating very small quantities of calcium. If reducing substances are present, the material may be ignited. S. I. L.

The Approximate Estimation of Magnesium in a Single Drop of Sea-water. G. DENIGÈS (*Compt. rend.,* 1922, **175**, 1206—1208).—The author describes the conditions under which the brown precipitate produced by the action of potassium hypoiodite on a solution containing magnesium-ions may be employed as a method for the colorimetric estimation of magnesium. Full experimental details are given (cf. *J.S.C.I.,* 1923, 207A). It is claimed that the method is rapid and sufficiently accurate for most purposes; moreover, a single drop only of the solution to be analysed for magnesium is required. H. J. E.

The Acidimetric Titration of Magnesium in its Salts. I. M. KOLTHOFF (*Rec. trav. chim.,* 1922, **41**, 787—794).—The potentiometric titration of solutions of magnesium salts by means of alkalis is tedious and can only be carried out in solutions of a concentration greater than 0·5*N*; even under the most favourable conditions the error lies between 1% and 2%. No greater accuracy is attained by titrating a magnesium solution of concentration 0·5*N* or greater with normal sodium hydroxide, using nitramine

as indicator. The method recommended is based on the addition of excess of alkali to the solution containing magnesium, which is then made up to a definite volume, shaken, and allowed to remain. An aliquot portion of the clear solution is then titrated for excess of alkali, which should not be present to a greater extent than 0·01*N*. The presence of calcium is not disadvantageous.
H. J. E.

A New Method of Estimating Cadmium. R. CERNATESCO (*Bull. Acad. Sci. Roumaine*, 1922, **8**, 43—46).—The cadmium is precipitated as sulphide by means of hydrogen sulphide and excess of the gas boiled off. A known volume of silver nitrate is added to the solution together with the precipitate, and the latter is blackened immediately, owing to the formation of silver sulphide. The whole is heated so as to complete the transformation, and the excess of silver nitrate determined by titration (cf. Mann, A., 1879, 1054). If chlorine is present, the precipitated cadmium sulphide must be separated by filtration through asbestos before the silver nitrate is added.
H. J. E.

The Titration of the Mercuric-ion with the Chlorine-ion, and its Application to the Analysis of Cinnabar and Organic Derivatives of Mercury. ÉMILE VOTOČEK and LADISLAV KAŠPÁREK (*Bull. Soc. chim.*, 1923, [iv], **33**, 110—122).—The method previously described for the mercurimetric estimation of chlorides may, conversely, be used for the estimation of mercury (cf. A., 1918, ii, 238, 272). The metal in the form of a mercuric salt of an oxygenated mineral acid is titrated in the cold with standard sodium chloride solution in presence of 0·06 g. of sodium nitroprusside per 200 c.c. volume of liquid. The titration is continued until the cloudiness due to mercuric nitroprusside just disappears, and under these conditions 1 c.c. of *N*/10-sodium chloride is equivalent to 0·010124 g. of mercury. For the estimation of mercury in mercuric sulphide or in cinnabar, about 0·3 g. of substance is digested with 50 c.c. of an oxidising mixture of 1 vol. of nitric acid with 2 vols. of sulphuric acid, and diluted to 1000 c.c. after complete decolorisation, 200 c.c. of the diluted solution being used for a titration. For the estimation of mercury in organic derivatives, the same treatment was successful in the aliphatic series, but in the aromatic and heterocyclic series nitric acid and powdered potassium permanganate were required to effect the destruction of the organic matter. Oxides of manganese in the reaction product were dissolved by the addition of sodium nitrite solution, excess of nitrous acid was eliminated by permanganate and sulphuric acid, followed by a few drops of oxalic acid to produce a colourless solution, which was then titrated with sodium chloride as above. When halogens are present it is, of course, necessary to precipitate the mercury as sulphide and redissolve the precipitate in the nitric-sulphuric acid mixture before proceeding to the titration. The direct titration is not disturbed by the presence of metals of which the nitroprussides are soluble in water, and mercury can accordingly be estimated

by this method in presence of alkali or alkaline-earth metals, of lead, zinc, aluminium, chromium, ferric iron, or manganese.

G. F. M.

Estimation of Iron in Ores and Silicate Rocks. F. R. ENNOS and R. SUTCLIFFE (*Summary of Progress Geol. Survey*, 1921, 174—176).—In the case of samples containing iron, aluminium, titanium, and phosphate, the weighed oxides of the aluminium group are fused with pyrosulphate and the titanium is estimated colorimetrically in the solution resulting from this fusion. The solution is then evaporated to a volume of about 100 c.c., the excess of hydrogen peroxide is destroyed by treating the hot solution with the required quantity of sulphurous acid, and the solution at 90° is saturated with hydrogen sulphide. The precipitate of sulphur and platinum sulphide (the platinum is derived from the crucible in which the fusion was made) is separated by filtration and washed with very dilute sulphuric acid. The filtrate is cooled, oxidised with dilute potassium permanganate solution, 10 c.c. of concentrated hydrochloric acid and 5 c.c. of 20% ammonium thiocyanate solution are added, and the iron is titrated with standardised titanium trichloride solution.

W. P. S.

The Separation of Iron and Zinc by Means of Bases. K. SCHERINGA (*Pharm. Weekblad*, 1923, 60, 39—43).—Addition of sodium hydroxide to a solution containing both zinc and ferric salts precipitates the two metals together, the weight of zinc oxide carried down varying with the amount of iron present, although not directly. Even if the zinc salt be added after the sodium hydroxide, the results are the same, nor could complete separation be effected in any way with this base. Precipitation with cold concentrated ammonia (25%) effects complete separation, if ammonia of the same strength be used to wash the precipitate.

S. I. L.

Successive Electrometric Titration of Iron, Uranium, and Vanadium. R. G. GUSTAVSON and C. M. KNUDSON (*J. Amer. Chem. Soc.*, 1922, 44, 2756—2761).—Analyses of salts of iron, vanadium, and uranium have been investigated by the electrometric method, individually and in all possible combinations, and a number of curves plotted indicating the results. Iron, vanadium, and uranium may each be titrated electrometrically after reduction with zinc and sulphuric acid, but in the case of vanadium the titration must be carried out in an indifferent atmosphere, such as carbon dioxide. A high concentration of acid favours sharp inflection points at all three end-points in the vanadium titration. Mixtures of salts of iron and uranium may be titrated with permanganate solution after reduction with zinc and sulphuric acid by the electrometric method, provided the acidity is kept low, the optimum concentration being about 5 c.c. of concentrated sulphuric acid to 250 c.c. of solution. Iron and vanadium in mixtures may be estimated by a similar method, using 10 c.c. of acid to 250 c.c. of solution, but in this case the titration must be made in an atmosphere of carbon dioxide to obtain trustworthy

results. The volume representing the vanadium is obtained directly from the final step in the curve, whilst that representing iron can be obtained by subtracting this value from the first step in the same curve. The estimation of vanadium and uranium in mixtures when 5—10 c.c. of sulphuric acid are present may be made by titrating the mixture in a non-oxidising atmosphere. The vanadium is obtained directly as before, and the uranium by difference. When all three elements, iron, vanadium, and uranium, are present, the estimation may be made similarly. It is best to use 4 c.c. of sulphuric acid to 250 c.c. of solution for the first part of the titration, and then, after the second inflection is obtained, a like quantity of acid is added and the titration continued. The vanadium and iron are represented by the last and the next to the last steps, respectively, whilst the uranium is again found by subtracting the value found for vanadium from the value indicated in the portion of the curve between the first and second inflections.

J. F. S.

Gravimetric and Volumetric Methods for the Estimation of Tin in Alloys. ANTONÍN JÍLEK (*Chem. Listy*, 1923, **17**, 7—11).—Two methods for the estimation of tin in alloys are examined, namely, the gravimetric method of Czerwek (*Z. anal. Chem.*, 1876, **15**, 505) and an iodometric method. Czerwek's method and its modifications for the analysis of bearing metals are closely studied. The following observations are made. The stanniphosphate precipitate should be washed with a mixture of acids similar to that used to dissolve the alloy, but with the addition of phosphoric acid, and not with nitric acid alone, as Czerwek recommends, otherwise antimonic acid, which is insoluble in nitric acid, would remain adsorbed on the precipitate. The solution of this precipitate in alkali sulphide should not be boiled very long, as a gelatinous precipitate containing stannic oxide and phosphoric oxide tends to separate with increase in hydroxyl-ion concentration. In the conversion of the stannous sulphide into stannic oxide, the sulphide should be moistened before the addition of nitric acid, as otherwise the violence of the reaction would lead to spattering of the contents of the crucible. A series of analyses of pure tin was carried out, reducing progressively the quantity of tin, but keeping the quantities of the reagents constant. As a result, it was found that with the quantities of the latter used [6 g. of acetic acid, 15 c.c. of nitric acid (*d* 1·4), 30 drops of 45% phosphoric acid, and 15 c.c. of water, followed by dilution with 300 c.c. of boiling water] the best results are obtained using 0·1 g. of tin. Should more be used, the results are high, whilst with less, precipitation of tin is slow and incomplete, so that using 0·0022 g. of tin, only 43% was found by this method. The stanniphosphate precipitate was examined, and its composition found to be roughly $2SnO_2 : P_2O_5$. This varies with the quantity of phosphoric acid used, and can contain adsorbed lead, copper, and antimony salts. For this reason, the tin cannot be estimated by weighing the stanniphosphate precipitate.

R. T.

New Method for the Electrometric Titration of Vanadium in the Presence of Iron and Chromium. H. H. WILLARD and FLORENCE FENWICK (*J. Amer. Chem. Soc.*, 1923, **45**, 84—92).—The electrometric titration of vanadium by means of ferrous sulphate solution and potassium permanganate solution has been investigated. It is shown that a polarised bimetallic electrode system affords a more sensitive means of determining the end-point in the reduction of vanadic acid by ferrous sulphate than the usual monometallic electrode. In acetic acid solution, the reduction of chromic acid by hydrogen peroxide in the presence of vanadic acid may be made selective and gives an excellent means of estimating the latter element in all alloy steels. Results may be obtained which agree to 0·005% when 5 g. samples are used; one advantage over the method involving selective oxidation of vanadium with nitric acid lies in the reduced period of boiling required. Traces of vanadium may be titrated directly in the presence of large quantities of phosphotungstate and phosphomolybdate. For the analysis of vanadium steels, the following procedure is recommended. *Chromium and chromium vanadium steel.* A sample requiring about 10 c.c. of 0·02*N*-ferrous sulphate is placed in a 600 c.c. beaker, 20—30 c.c. of water are added and the calculated quantity of concentrated sulphuric acid is added from a burette. Each gram of steel requires 1·0 c.c. of this acid and a 4·0 c.c. excess to effect rapid solution. The beaker is heated gently until the sample is dissolved and salts commence to separate. The solution is then diluted with 20 c.c. of hot water and warmed until clear, when 4—5 c.c. of concentrated nitric acid are added cautiously and the solution is boiled. The oxidation of the iron and vanadium is completed with a slight excess of a solution of potassium permanganate. Sufficient sodium acetate is added to combine with the sulphuric acid in excess over that required for solution of the steel (1 c.c. concentrated sulphuric acid$\equiv$4·8 g. of sodium acetate trihydrate) and 40—50 c.c. of glacial acetic acid. Then 0·5 g. of neutral sodium perborate is added, the solution diluted to 200 c.c., and boiled for twenty minutes. The solution is cooled to the ordinary temperature, 25—30 c.c. of concentrated hydrochloric acid are added and titrated with 0·02*N*-ferrous sulphate solution, using a bimetallic system to ascertain the end-point (this vol., ii, 33). *Chromium vanadium molybdenum steels* are treated in exactly the same way. *Chromium vanadium tungsten steels.* The sample is treated with 40 c.c. of hydrochloric acid (3 : 1), and heated until action ceases. Then 8—10 c.c. of concentrated nitric acid are added drop-wise, and when the first violent action has ceased the solution is evaporated to 20 c.c. It is then diluted with hot water and boiled to dissolve soluble salts, filtered, and the residue washed with 2% hydrochloric acid. The filtrate is oxidised with potassium permanganate and the free acid neutralised by a sufficient excess of sodium acetate (1 g. of hydrochloric acid$\equiv$3·73 g. of sodium acetate trihydrate). From this point the analysis is as described above. A small quantity of vanadium is occluded by the tungstic acid; to estimate this,

the tungstic acid is dissolved in sodium carbonate solution and boiled for ten minutes with about 0·5 g. of perborate. It is then acidified with 3—5 c.c. of phosphoric acid and 25—40 c.c. of sulphuric acid (3 : 1) and titrated electrometrically to the permanent drop in potential. J. F. S.

Detection of Antimony and Tin in Qualitative Analysis. E. RUPP (*Ber. Deut. pharm. Ges.*, 1922, **34**, 334—335).—A modification of the usual test for antimony in presence of tin (by means of platinum foil and granulated zinc) is described in which the platinum foil is replaced by a very small piece of platinum wire. Details are also given of a method in which the platinum is entirely dispensed with, being replaced by a piece of iron wire, by which it is claimed that 0·08 mg. of antimony can be detected with certainty. P. M.

Interferometric Analysis of Liquid Mixtures of Organic Substances. ERNST COHEN and H. R. BRUINS (*Z. physikal. Chem.*, 1923, **103**, 337—348).—The authors have investigated the difficulties which arise when the Rayleigh-Löwe water interferometer is used for the analysis of solutions of organic liquids. It is shown that when using this instrument with organic liquids the upper interference band undergoes a lateral displacement and becomes diffuse, whilst the bands are oblique and bent and continuously change their form. These changes are due to the influence of temperature on the refractive index of the solvent, the vaporisation of the liquid and condensation on the cover glass, the absorption of water from the air during the placing of the liquid in the observation vessels, and the index of refraction of the bath liquid. Each point has been subjected to careful experiment and precautions for eliminating the disturbance in each case are indicated. When all these precautions are taken, the water interferometer gives results which are as sharp and as exact as those obtained with aqueous solutions. J. F. S.

Estimation of Thymol in Thyme Oil. HUGO MASTBAUM (*Anal. Fis. Quim.*, 1922, **20**, 501—504).—Phenols are extracted from thyme oil by repeated shaking with sodium hydroxide solution. On addition of strong hydrochloric acid to an aliquot portion of the extract, the phenols separate. The thymol is obtained by crystallisation and weighed after collection and drying. G. W. R.

Colorimetric Estimation of Pyrogallol, Gallotannin, and Gallic Acid. C. AINSWORTH MITCHELL (*Analyst*, 1923, **48**, 2—15).—The method is based on the fact that a solution containing 0·1% of ferrous sulphate and 0·5% of sodium potassium tartrate reacts immediately with gallotannin to form a soluble compound which, unlike the ink formed with ferrous sulphate alone, is fairly stable. The coloration ranges from reddish- to bluish-violet, it is apparently specific for the pyrogallol grouping,

and its intensity is proportional to the amount of this tinctogenic group in gallic acid and the various tannins. Thus the colour factor for gallic acid referred to pyrogallol is identical with the ratio of their molecular weights, namely 1 : 1·5 for crystalline gallic acid, and 1 : 1·36 for the anhydrous acid. Owing to its greater stability, it is preferable to use solutions of gallic acid rather than of pyrogallol as the standard for comparison, and in the estimation of the natural gallotannins the gallic acid equivalent is determined colorimetrically and this must then be multiplied by a suitable factor to obtain the absolute amount of gallotannin. Owing to the uncertainty of the constitution of these substances, this factor can only be obtained empirically, and it varies with different varieties; for Aleppo galls, for example, the factor 1·85 was found suitable, whilst for the tannin in Chinese galls the factor 2·1 is appropriate. For the estimation of the tinctorial value of a tannin it is, however, unnecessary to use these factors at all, the pyrogallol equivalent expressing all that is required. Based on the hypothesis that the colour intensity is always a measure of the pyrogallol groups present, it is suggested that the average "pure" gallotannin is a mixture of different glucosides, but mainly of di-digalloyl glucose, with a digallic anhydride of the type described by Nierenstein (*J. Soc. Chem. Ind.*, 1922, 29T). Such a mixture would yield the required proportion of dextrose and contain the necessary pyrogallol groups to give the observed coloration with the ferrous tartrate reagent. Most natural gallotannins contain a proportion of gallic acid, and each can be colorimetrically estimated by estimating the two substances together first in terms of gallic acid, then precipitating the gallotannin by means of quinine hydrochloride, and finally estimating the gallic acid in the filtrate, the difference between the two results multiplied by the appropriate factor giving the amount of gallotannin. The results of the estimation of gallic acid and gallotannin in numerous commercial varieties of nut galls, including white and roasted galls, and also in myrobalans and various other materials containing tannin such as tea, are given. G. F. M.

Estimation of the Admixed Arachidic and Lignoceric Acids in Peanut Oil by means of Magnesium Soaps. Arthur W. Thomas and Chai-Lan Yu (*J. Amer. Chem. Soc.*, 1923, 45, 113—128).—The authors have made a systematic and quantitative study of the behaviour of a number of pure soaps in various solvents, and in particular the solubilities of the magnesium soaps of various fatty acids in 90% (by volume) ethyl alcohol have been measured. At 25°, 100 g. of the alcohol dissolve 0·007 g. of magnesium stearate, or 0·006 g. of magnesium lignocerate, but 8·60 g. of magnesium oleate. The results indicate that an excellent separation of magnesium stearate, arachidate, and lignocerate from magnesium oleate, linolate, and linolenate is possible by means of this solvent. Under the same conditions, 100 g. of 94·3% (by volume) alcohol dissolve 0·633 g. of potassium stearate, 0·153 g. of potassium lignocerate, or 41·1 g. of potassium oleate. The

solubilities of stearic and lignoceric acids in three strengths of alcohol have been determined and the results show that a quantitative separation of arachidic and lignoceric acids from other saturated acids can best be accomplished with 90% (by volume) alcohol after remaining for one night at 20° or 25°.

A new method for the estimation of peanut oil based on the above separation of the magnesium soaps of saturated and unsaturated acids is outlined as follows: 10 g. of the oil are saponified by boiling with a mixture of 50 c.c. of 5% alcoholic potassium hydroxide and 50 c.c. of 95% alcohol for half an hour. The soap solution, while still warm, is neutralised with 20% alcoholic acetic acid and then made just alkaline with the alcoholic potassium hydroxide, using phenolphthalein as indicator. To this solution, 25 c.c. of alcoholic magnesium acetate (50 g. of magnesium acetate dissolved in 100 c.c. of water, heated to boiling, and filtered and the filtrate diluted with three volumes of 95% alcohol) are added and the mixture is heated to boiling and left over-night at 10°. The insoluble soaps are collected and washed with 30 c.c. of 90% alcohol. These insoluble soaps are then hydrolysed by boiling with 100 c.c. of 5*N*-hydrochloric acid for five minutes. Cold water is added to precipitate the solid acids, which are collected and washed free from magnesium and chlorine. The solid acids are extracted with three successive portions of 20 c.c. of warm 90% alcohol and the solution left over-night at 20° or 25°. The crystals which form are separated and washed twice with 10 c.c. of 90% alcohol and then with 70% alcohol until the washings give no turbidity with water. The filtrate and washings are collected and measured. The solids are washed with alcohol into a weighed beaker; the solvent is evaporated and the residue dried at 80° and weighed. This weight is corrected for the weight of lignoceric and arachidic acids which remain dissolved in the filtrate and washings of 90% alcohol. In estimations of known mixtures of peanut oil with olive oil or cotton-seed oil, the error did not exceed 5% of the value found for the peanut oil. The percentage of arachidic and lignoceric acids in peanut oil are taken as 5% on an average.

Time and work may be saved by using the solution left after the ordinary determination of the saponification number, for the above procedure, if a high order of accuracy is not required.

The proposed method is not intended for the separation of saturated acids from all unsaturated acids in all fatty oils, as magnesium erucate and an unsaturated magnesium soap from tung oil (probably eleomargarate) were found to be insoluble in 90% alcohol (cf. following abstract). W. G.

New Qualitative Tests for Rape and Tung Oils. ARTHUR W. THOMAS and CHAI-LAN YU (*J. Amer. Chem. Soc.*, 1923, **45**, 129—130).—Rapeseed oil is subjected to the method of analysis outlined for peanut oil (cf. preceding abstract), and the acid cake left after hydrolysis of the magnesium soaps is dissolved in 60 c.c. of 90% alcohol and the solution is left over-night at 20° or 15°.

Any crystals which may have formed are filtered off and discarded and the filtrate and washings evaporated to dryness and the m. p. or acid number, or preferably the iodine number, of the residue is determined. Two samples of genuine rapeseed oil, thus treated, yielded about 25% of the final acid product having m. p. 35° (erucic acid has m. p. 32°), iodine number 70—72 (erucic acid has 74·99).

In the case of tung oil, the insoluble magnesium soaps are collected while hot, washed with 90% alcohol, and decomposed with dilute hydrochloric acid in the absence of air. The liberated acid has a strong odour characteristic of tung oil. It is soluble in cold 90% alcohol and melts at about 44°. After one or two days' contact with air it absorbs oxygen and gradually changes to a dark brown, resinous mass. The yield of this acid (eleomargaric) obtained from one sample of tung oil tested was about 20%. W. G.

The Estimation of Chloral Hydrate. I. M. Kolthoff (*Pharm. Weekblad*, 1923, **60**, 2—8).—In the ordinary method, in which the chloral is converted by excess of sodium hydroxide into chloroform and sodium formate, and the excess of alkali titrated with standard acid, the results are always high; this has been attributed to action of the excess of alkali on the chloroform produced. The error is in fact due to absorption of carbon dioxide from the air by the alkali during the time required for the reaction, and if decinormal sodium hydroxide is used, the mixture may be allowed to remain at 40° for twenty minutes without decomposition of the chloroform. Accurate results are obtained by allowing 30 c.c. of $N/10$-sodium hydroxide to act on 25 c.c. of 0·1 molar chloral hydrate solution for fifteen minutes in a closed flask, and then titrating the excess, using phenolphthalein; the alkali must be standardised by carrying out the same procedure.

The iodine method of Rupp (A., 1903, ii, 699), in which the aldehyde is oxidised to trichloroacetic acid by excess of iodine, the latter being titrated back in the usual way, gives poor results if sodium hydroxide is used, as proposed by Rupp. Good results are obtained by adding 2 c.c. of N-sodium carbonate and 10 c.c. of 0·1 molar chloral hydrate to 25 c.c. of $N/10$-iodine solution, leaving one hour in a closed vessel, adding hydrochloric acid, and titrating with thiosulphate.

The chloral hydrate for the work was standardised by Wallis's method (A., 1906, ii, 255) as modified by van Rossum (A., 1908, i, 501), *i.e.*, complete hydrolysis to sodium chloride and sodium formate by heating with sodium hydroxide in a sealed tube, and gravimetric estimation of the chloride.

Bromine in acid solution will not oxidise chloral, which therefore must have a much greater reducing power in alkaline than in acid solutions. S. I. L.

A New Test for Acraldehyde and Its Bearing on Rancidity in Fats. Wilmer C. Powick (*J. Ind. Eng. Chem.*, 1923, **15**, 66).—To a few drops of dilute acraldehyde solution in a test-tube, a drop of 3% hydrogen peroxide is added, and after about one

minute 5 c.c. of concentrated hydrochloric acid are added, and the test-tube is shaken. On shaking with 5 c.c. of a 1% ethereal solution of phloroglucinol, a deep red colour is imparted to the aqueous layer, showing a fairly narrow absorption band in the yellow-green. The red colour is not obtained in the absence of hydrogen peroxide, whilst if there be an excess of acraldehyde a purple precipitate is obtained. This test differs from the Kreis test for rancidity in fats by the addition of the hydrogen peroxide, and under these conditions no coloration is given by the saturated aldehydes or by crotonaldehyde. The spectrum given by the substance formed in the Kreis test is identical with that obtained as above, and it therefore seems that the substance responsible for this test in rancid fats is identical with that produced by the action of hydrogen peroxide on acraldehyde. P. M.

Use of Schiff's Reagent for the Estimation of Acraldehyde. CHARLES MOUREU and ÉTIENNE BOISMENU (*J. Pharm. Chim.*, 1923, [vii], **27**, 49—54, 89—97).—Acraldehyde can be accurately estimated colorimetrically by means of Schiff's reagent by adopting the following procedure: a standard solution of acraldehyde containing 0·5 g. per litre is prepared from the freshly distilled substance by collecting in an ampoule, sealing, and weighing, and then breaking in the requisite quantity of water to give a solution of the required strength. One arm of each of two inverted **Y**-tubes is filled respectively with 10 c.c. of this standard solution, and 10 c.c. of the unknown acraldehyde solution, diluted to contain slightly less than 0·05% of acraldehyde. The other arms are then filled with 5 c.c. of Schiff's reagent, the tubes are closed with glass stoppers and simultaneously inverted, thereby mixing the reagent with the two solutions at the same moment. For the attainment of the maximum intensity of coloration twenty-five minutes are allowed before examining the tints in the colorimeter. The height of the standard solution having the same intensity of coloration as 25 mm. of the solution under test is measured, and the acraldehyde content of the latter may be read off directly from the curve provided, which may be reconstructed from the following figures: where I is the height of standard solution in mm. and II the concentration of acraldehyde in mg. per litre in unknown solution.

I.	25	22	20·6	18·8	15·5	12·8	10·3
II.	500·0	476·2	454·5	434·8	400·0	370·4	333·3

It will be seen from these figures that on diluting a solution of acraldehyde the intensity of coloration is lowered more rapidly than the acraldehyde content. The whole of the above procedure must be carried out with cold solutions, as at higher temperatures the colours obtained are never comparable, but consist of a mixture of colours tending towards green with varying velocities with solutions of varying concentrations. The presence of stabilisers, such as pyrogallol, pyrocatechol, quinol, or gallic acid, does not interfere with the colorimetric estimation. G. F. M.

The Estimation of Acetone in Methyl Alcohol and the Purification of Methyl Alcohol by Sodium Hypoiodite. HENRY HUTCHINSON BATES, JOHN MYLNE MULLALY, and HAROLD HARTLEY (T., 1923, **123**, 401—404).

Estimation of Acetone in Methyl Alcohol. ELLA SÖDERLUND (*Svensk. Kem. Tidskr.*, **34**, 152—157; from *Chem. Zentr.*, 1922, iv, 1074—1075).—A modification of the method of Messinger (A., 1889, 313). Ten c.c. of methyl alcohol are diluted to 100 c.c.; 10 c.c. of this solution are treated in a stoppered flask with 25 c.c. of sodium hydroxide solution. A large excess of 0·1*N*-iodine solution is added, and after keeping in darkness for ten minutes 26 c.c. of *N*-sulphuric acid are added. The excess of iodine is estimated by titration with thiosulphate. G. W. R.

Rapid Volumetric Method of Estimating Acetone. M. MARQUEYROL and P. LORIETTE (*Mém. des Poudres*, 1922, **19**, 362—367).—The method depends on the action of sodium hypoiodite on acetone in alkaline solution whereby iodoform and sodium acetate are produced. The hypoiodite is formed by the interaction of potassium iodide and sodium hypochlorite. Commercial eau de Javel is used, and is standardised against pure acetone, 10 c.c. of which are dissolved in water and made up to 1 litre. Ten c.c. of this solution are diluted with 90 c.c. of water and 10 g. of potassium iodide and 20 c.c. of sodium hydroxide (*d* 1·325) added. The hypochlorite is run in from a burette with constant agitation, and the solution tested with an outside indicator consisting of 1 g. of starch, 10 g. of sodium hydrogen carbonate and 100 c.c. of water. The end-point is very sharp and is heralded by the precipitation of flocks of iodoform. In estimations of acetone, the acetone is distilled into a 500 c.c. measuring flask, and 100 c.c. are taken for the estimation, which is carried out as described above. The presence of alcohol, aldehyde, diphenylamine, or ammonia does not affect the titration. Substituted carbamides, however, give traces of iodoform, which can usually be neglected. H. C. R.

Estimation of Reducing Sugars by Means of Fehling's Solution with Methylene-blue as Internal Indicator. J. HENRY LANE and LEWIS EYNON (*J. Soc. Chem. Ind.*, 1923, **42**, 32—37T).—In the volumetric estimation of sugars by means of Fehling's solution the disadvantages attending the use of an external indicator can be altogether avoided by using a 1% solution of methylene-blue as internal indicator. So long as any copper remains unreduced, the indicator retains its colour, but it is immediately decolorised by the sugar the moment all the copper is reduced. The action is reversible. To attain the maximum of accuracy, consistent procedure is necessary, in combination with conversion tables based on the same method of operation. The following standard method of titration is recommended: 10 c.c. or 25 c.c. of Soxhlet's modification of Fehling's solution are measured into a 300 c.c. flask and treated cold with almost the whole of the sugar solution (determined by a preliminary trial) required to effect

reduction of all the copper. The liquid is then heated to boiling, kept in moderate ebullition for two minutes, and then, without removing the flame, 3—5 drops of the indicator are added and the titration is completed in one minute further so that the liquid is boiled in all three minutes. The end-point can be determined generally to within 1 drop of the sugar solution. Based on this method of procedure tables have been drawn up giving the weight in mg. of sugar required to reduce the volume of Fehling's solution employed. This factor varies appreciably with the concentration of the sugar solution, and values are given for volumes of 15—50 c.c. Tables are given for invert-sugar, both in presence and absence of sucrose, for dextrose, lævulose, maltose, and lactose. G. F. M.

Estimation of Dextrose in Cerebrospinal Fluid. J. LANZA (*Anal. Fis. Quím.*, 1922, **20**, 400—402).—The method is based on the reaction whereby picric acid and dextrose in alkaline solution give picramic acid, $OH\cdot C_6H_2(NO_2)_2\cdot NH_2$, which is distinguished by its red colour. To 2 or 3 c.c. of the cerebrospinal fluid, picric acid in the proportion of 0·05 g. for each c.c. of liquid used is added. After warming, the liquid is rapidly cooled and centrifuged. Dextrose is then estimated colorimetrically by comparison with a standard dextrose solution in a Duboscq colorimeter. G. W. R.

The Tryptophan-Aldehyde Reaction. ERNST KOMM and EBERHARD BÖHRINGER (*Z. physiol. Chem.*, 1923, **124**, 287—294).—A new modification of the aldehyde test for tryptophan is described One c.c. of the solution of tryptophan is added to a 15% solution of hydrochloric acid containing, in 500 c.c., 6 c.c. of a 0·1% solution of formaldehyde. To the mixture are added 10 c.c. of concentrated sulphuric acid. The whole is shaken and allowed to cool. The colour produced is stable, and proportional to the tryptophan present, for the colorimetric estimation of which the reaction may be applied. It is sensitive to a solution of tryptophan containing 1 part in 175,000 parts. W. O. K.

Modification of the Moreigne Ureometer. J. LANZA (*Anal. Fis. Quím.*, 1922, **20**, 403—405).—A modification of Moreigne's apparatus for the estimation of urea by the hypobromite method is described. G. W. R.

The Hydrocyanic Acid Question. XI. The Detection of Hydrocyanic Acid in Plants. L. ROSENTHALER (*Schweiz. Apoth. Ztg.*, 1922, **60**, 477—481; from *Chem. Zentr.*, 1922, iv, 1124—1125; cf. A., 1922, i, 614—615).—Hydrocyanic acid in plants may be detected by its decolorisation of blue starch-iodide solution. In the presence of essential oils which contribute iodine the plant material should first be extracted with ether. Where only traces of hydrocyanic acid are to be expected, it may be removed from the material by long passage of a stream of air and collected in mercuric chloride solution. By addition of potassium iodide to the mercuric chloride solution with subsequent passage of carbon dioxide or warming with sodium hydrogen carbonate,

the hydrocyanic acid is again liberated. For the detection of hydrocyanic acid in plant sections, the starch-iodide method is suitable. G. W. R.

Analysis of the Products of Hydrolysis of Cyanamide by Acids. A. GRAMMONT (*Bull. Soc. chim.*, 1923, [iv], **33**, 123—128).—A satisfactory evaluation of fertilisers derived from cyanamide requires, not only an estimation of organic and ammoniacal nitrogen, but also that the former should be differentiated into carbamide nitrogen, dicyanodiamide nitrogen, and dicyanodiamidine nitrogen, as these substances have widely different values as fertilisers, and some are even toxic. Such discrimination between the forms of combination of the nitrogen present is obtained by the following method of assay: Total nitrogen is estimated by Kjeldahl's method; ammonia by converting the ammonium salts present in solution of the material, neutralised to phenolphthalein with dilute sodium hydroxide, into hexamethylenetetramine by the addition of formaldehyde, and titrating the liberated acid with standard alkali hydroxide; carbamide by precipitation by the Fosse method with xanthydrol as dixanthylcarbamide, and weighing as such; dicyanodiamidine by precipitation as its nickel compound, $Ni(C_2H_4ON_4)_2,H_2O$, by the method of Dafert and Miklomb, washing the precipitate with 2% ammonia, drying at 100° and weighing; and finally arriving at the amount of dicyanodiamide by difference, as cyanamide itself is always absent. If the fertiliser contains phosphoric acid or soluble phosphates they must first be removed by adding sodium hydroxide solution to the material after digesting for one hour in water until neutral to phenolphthalein, whereby soluble phosphates are precipitated as calcium phosphate. The above estimations are then carried out on the filtrate. G. F. M.

The Interconvertibility of Creatine and Creatinine. III. The Estimation of Creatinine and Creatine in Blood-serum. AMANDUS HAHN and GEORG MEYER (*Z. Biol.*, 1922, **76**, 247—256; cf. A., 1921, i, 517).—In the estimation of creatine in blood-serum, trichloroacetic acid is very suitable for precipitating the proteins. Fifty c.c. of serum are diluted with 25 c.c. of water, and 50 c.c. of a freshly prepared 10% solution of trichloroacetic acid are added. The creatine in the filtrate is then estimated by conversion into creatinine by treatment at 60—65° with hydrochloric acid, and estimated along with the preformed creatinine as previously described (*loc. cit.*). In the estimation of the preformed creatinine, colloidal ferric hydroxide may be conveniently used as a protein precipitant. W. O. K.

Purification of Picric Acid for Creatinine Estimations. STANLEY R. BENEDICT (*J. Biol. Chem.*, 1922, **54**, 239—241).—Recrystallisation from benzene is recommended. Folin and Doisy's method (A., 1917, ii, 159) is unsuitable. E. S.

Colorimetric Estimation of Cystine in Urine. JOSEPH M. LOONEY (*J. Biol. Chem.*, 1922, **54**, 171—175).—Folin and Looney's method (A., 1922, ii, 539) for the estimation of cystine is applied

directly to urine. The coloration due to the presence of uric acid and other reducing substances is corrected for by making an estimation without the addition of sodium sulphite to the urine and subtracting the resulting value from that obtained in the presence of sodium sulphite. A cystine standard is used in each case. The readings must be made not later than eight minutes after the addition of the phosphotungstic acid reagent. E. S.

Colorimetric Method for the Estimation of Cystine. EUGEN HERZFELD (*Schweiz. med. Woch.*, 52, 411—412; from *Chem. Zentr.*, 1922, iv, 1076).—The method consists in precipitating the sulphur from an alkaline solution of cystine by addition of copper sulphate solution. After freeing the precipitated copper sulphide from copper oxide by treatment with dilute sulphuric acid, it is dissolved in nitric acid and by addition of ammonia converted into a solution suitable for colorimetric estimation. For comparison, a solution is prepared from a known weight of pure cystine. Experimental details of the method are given. G. W. R.

Estimation of Morphine. JOHN RALPH NICHOLLS (*Analyst*, 1922, **47**, 506—510).—A general method for the extraction of morphine is described. One volume of the morphine solution is mixed with 1 volume of alcohol, the mixture is rendered ammoniacal and shaken with 1 volume of chloroform. The chloroform layer is drawn off, and the mixture is again shaken with the addition of 0·5 volume of alcohol and 1 volume of chloroform. This process of extraction is made three or four times, the combined extracts are then evaporated, the residue is dissolved in a definite volume of standardised acid, the solution diluted to a known volume, and the morphine is then estimated volumetrically, colorimetrically, or polarimetrically. W. P. S.

System of Blood Analysis. Supt. IV. Revision of the Method for Estimating Uric Acid. OTTO FOLIN (*J. Biol. Chem.*, 1922, **54**, 153—170).—The various recent methods for the estimation of uric acid in blood are reviewed, and the author's method (A., 1919, ii, 308) is modified. The procedure now adopted is, in its essentials, similar to that of Benedict (A., 1922, ii, 403) except that the uric acid reagent of Folin and Denis is retained. The original precipitation method is retained in a modified form as a check on the direct method. Contrary to Pucher's statement (A., 1922, ii, 668), 90—100% of added uric acid can be recovered from the tungstic acid filtrate; the heat process recommended by this author gives irregular results and should be avoided. E. S.

Estimation of Uric Acid. STANLEY R. BENEDICT (*J. Biol. Chem.*, 1922, **54**, 233—238).—Mainly a reply to Folin (cf. preceding abstract). E. S.

General and Physical Chemistry.

Variation of the Refractive Index of Oxygen with Pressure, and the Absorption of Light by Oxygen at High Pressures. (MISS) H. I. EADIE and JOHN SATTERLY (*Trans. Roy. Soc. Canada*, 1922, **16**, III, 63—73).—Gladstone and Dale's law for the relation of refractive index to density has been confirmed in the case of oxygen for pressures ranging from 2·1 to 140 kg. per sq. cm. Evidence for the existence of absorption in oxygen at pressures up to 100 atmospheres, in the regions λλ 6285, 5800, and 5350 Å. was not conclusive. J. S. G. T.

Variation of the Index of Refraction of Water, Ethyl Alcohol, and Carbon Disulphide with the Temperature. ELMER E. HALL and ARTHUR R. PAYNE (*Physical Rev.*, 1922, **20**, 249—258).—Measurements were made with a precision spectrometer, the construction and use of which are described. The two prisms used were of gold-plated brass, and optical glass sides, and had an angle of 60° and 75°, respectively; the temperature of the bath could be maintained indefinitely within 0·1° of any desired point. From tables showing the index of refraction of water relative to air, and the absolute index of refraction of water (both for sodium light), respectively, the following values are abstracted: 15°, 1·33341, 1·33377; 20°, 1·33299, 1·33327; 100°, 1·31783, 1·31819 (all ±0·00002). When reduced to a vacuum, the experimental values for pure water are well represented by the empirical formula $n=1\cdot33401-10^{-7}(66t+26\cdot2t^2-0\cdot1817t^3+0\cdot000755t^4)$. The temperature coefficient, dn/dt, at the temperatures mentioned has the values −0·00008, −0·00009, and −0·00030.

Corresponding values of the index of refraction, relative to air, and of the temperature coefficient, dn/dt, of ethyl alcohol (Kahlbaum's, 99·8% absolute) are abstracted as follows: 14°, 1·36290, (15°) −0·00040; 24°, 1·35885, (25°) −0·00041; 76°, 1·33626, (75°) −0·00046. For carbon disulphide, 15°, 1·62935, −0·00077; 20°, 1·62546, (25°) −0·00081; 45°, 1·60499, −0·00083. Although the absolute values obtained differ somewhat from those given by others for pure samples, the temperature coefficients are probably not affected by the slight amount of impurity present. For ethyl alcohol between 15° and 70°, the results correspond with the empirical equations $dn/dt=-10^{-6}[404+0\cdot44(t-15)+0\cdot0075(t-15)^2]$; for carbon disulphide between 15° and 45° $dn/dt=-10^{-6}[766+5\cdot12(t-15)-0\cdot105(t-15)^2]$. A. A. E.

The Secondary Spectrum of Hydrogen. E. GEHRCKE and E. LAU (*Sitzungber. Preuss. Akad. Wiss. Berlin*, 1922, **32**, 453—458).—The secondary spectrum of hydrogen has been obtained almost free from the Balmer series by using a discharge tube silvered on the inside. The bands in the red-yellow and the yellow-green portion of the spectrum consist of a number of lines arranged

symmetrically about a middle point, but the middle line about which the other lines are grouped is missing. The distances between the principal line and its α- and β-companions stand in the relationship 1 : 2; the δ line divides up the distance between the principal line and α in the proportion 2 : 3. The distance between the principal lines of the successive bands shows that the series approximates to a system of $\Delta\lambda$-bands, and, in this respect, they are similar to the resonance spectrum of sodium. In the bands in the blue-green region, the companions of the principal lines show a 3 : 2 relationship in their distances. The lines lying in the regions between the bands form symmetrical groups, and repetition of similar groups frequently occurs.

By the introduction of a spark gap into the discharge tube, the relative intensities of the hydrogen lines are very much altered. The change is in many respects similar to that observed by Merton when helium is mixed with hydrogen. The lines in the secondary spectrum are much sharper than the H_α line in the Balmer series. From the thickness of the lines it is deduced that the secondary spectrum owes its origin to molecular hydrogen (H_2, H_3, and H_4). The thickness of the lines increases with increase in the diameter of the tube owing to the higher temperature in the narrower tubes.

From the absence of the secondary spectrum in the light from the stars, it is concluded that the hydrogen giving rise to the Balmer series is always contaminated with other gases, and it is possible that it exists in the state of dissociated water vapour.

W. E. G.

Band Spectrum in the Arc Spectrum of Silicon. C. PORLEZZA (*Atti R. Accad. Lincei*, 1922, [v], **31**, ii, 513—517).—The author's examination of the arc spectrum of silicon gives results differing little from those of Gramont and Watteville (A., 1908, ii, 909), but showing a band spectrum not previously observed.

T. H. P.

Relative Intensities of the Stark Effect Components in the Helium Spectrum. JOHN STUART FOSTER (*Physical Rev.*, 1922, **20**, 214—220).—By the use of a discharge tube of the type first employed by Lo Surdo, the relative intensities of Stark effect components have been measured by means of a neutral wedge. Spectrograms were taken of the p and s components in turn, using a five-prism spectrograph; energy distribution curves were then calculated from the contour of the images and the corresponding wedge densities, and the relative intensities obtained by integration. The results for the main p components are: λ 4388, 8·2 (isolated), 4·1, 19·2, 28·0; λ 4472, 168, 694; λ 4922, 9·7, 31·6. Corresponding results for the s components are: λ 4388, 1·0 (isolated), 3·0, 11·3, 9·5; λ 4472, 76, 464; λ 4922, 6·2, 21·4.

A. A. E.

The Band Spectrum Associated with Helium. YUTAKA TAKAHASHI (*Proc. Phys. Math. Soc. Japan*, 1922, **4**, 187—193).—The band spectrum of helium consists of two double-headed bands, the lines of which form series for which Fowler has derived formulæ

of the Hicks type. Band spectra are usually attributed to molecules and not to atoms. It is possible, however, to assume that under certain conditions unstable helium molecules may exist from which the observed band spectrum may originate. A mathematical analysis shows that the form of a helium molecule is such that two nuclei, each accompanied by one electron about it, are connected by means of an electron and form something like a nucleus around which the remaining electron describes its orbit.

CHEMICAL ABSTRACTS.

Arc, Spark, and Absorption Spectra of Argon. W. W. SHAVER (*Trans. Roy. Soc. Canada*, 1922, **16**, III, 135—144).—The radiation produced in argon by electronic bombardment with an accelerating potential of 10·1 volts has been detected photographically and shown to consist of wave-lengths 4335·4, 4300·2, 4259·8, 4198·4, 4158·7, and 4055·9 Å. With accelerating fields ranging from 16 to 30 volts, the lines in the arc spectrum corresponded with those of the red argon spark spectrum. At 31 volts, the blue or enhanced spectrum began to appear, and at 54 volts, all the enhanced lines predicted by Bohr's theory were found. No new lines appeared when the potential was increased to 240 volts. No evidence of absorption was detected in the spectrum of ionised argon at pressures of 155, 5, and 2 mm. of mercury between wave-lengths 7000 Å. and 2150 Å., or in the spectrum of argon at 102·4 atmospheres pressure in the same region. J. S. G. T.

The Arc Spectra of Metals in Different Media and in a Vacuum. ST. PROCOPIU (*Compt. rend.*, 1923, **176**, 385—388).—In continuation of the work on mercury (A., 1922, ii, 600), the author has studied the arc spectra of copper, gold, zinc, cadmium, magnesium, calcium, aluminium, and carbon in air, hydrogen, coal gas, nitrogen, under water, and in a vacuum. As in the case of mercury, in the arc spectra of the metals under water, in coal gas, and in hydrogen the rays of the arc series become much broadened, and those of the higher order are weakened or disappear. In addition, spark rays appear. In nitrogen, the arc is stable with all the metals, and the rays appear to be greater in number than in air. Certain rays previously only found in a vacuum appear. The radiated energy is displaced towards the last terms of the arc series. Numerous rays are inverted. The spark rays are weakened. In a vacuum, the arc is stable in all cases. The last terms are more intense than in the other media. The energy radiated is displaced towards the ultra-violet. Numerous rays, particularly the cathodic rays, are inverted, and the rays are broadened. The arc in a vacuum shows enhanced rays, and for the most part they are spontaneously inverted. W. G.

Series Regularities in the Arc Spectrum of Chromium. C. C. KIESS and HARRIET KNUDSEN KIESS (*Science*, 1922, **56**, 666).—The arc spectrum of chromium contains at least three sets of series of which the members are triplets, two sets being composed of wide triplets, and one of narrow triplets. A constant difference

exists between the wave-numbers of homologous members of the wide-triplet series. Each component of the first member of the diffuse series is itself a narrow triplet. The principal, sharp, and diffuse series of the two parallel systems give values for $\Delta\nu$ of 112·44, 81·38; 112·45, 81·35; 112·78, 81·29; and 115·10, 91·42; 115·2, 91·3; 115·16, 91·54, respectively, whilst the narrow triplets are characterised by the frequency differences $\Delta\nu_1=8{\cdot}80$ and $\Delta\nu_2=5{\cdot}65$. A. A. E.

The Optical Spectrum of Hafnium. H. M. HANSEN and S. WERNER (*Nature*, 1923, **111**, 322; cf. A., 1922, ii, 463).—The optical spectrum of a large number of preparations containing hafnium has been examined and compared with that of a specimen of very pure zirconium prepared by Coster and Hevesy from commercial zirconium by removing the hafnium content. A table gives the wave-lengths and intensities of a number of lines, some of which have been observed by earlier investigators and ascribed to zirconium. There was, however, not the slightest trace of any of the lines ascribed by Urbain to an element, celtium, belonging to the family of rare earths, although this element has recently been assumed to possess the atomic number 72. A. A. E.

The *K* Absorption Spectrum of the Element 72 (Celtium). M. DE BROGLIE and J. CABRERA (*Compt. rend.*, 1923, **176**, 433—434).—Dauvillier has described in a preparation of celtium the presence in the spectrum of several feeble lines undoubtedly belonging to the element of atomic number 72, the presence of which has recently been recorded in several zirconium minerals by Coster and Hevesy. The absorption spectra of *X*-rays is an excellent means of revealing an element by its discontinuity *K*, and this method when applied to some minerals has shown the presence of the new element of atomic number 72. W. G.

The High Frequency Spectrum of Celtium. A. DAUVILLIER (*Compt. rend.*, 1923, **176**, 676—679).—A reply to Coster and von Hevesy's criticism (this vol., ii, 80, 171) of the author's attribution to celtium of the lines 1319·4 and 1561·8 X observed in a preparation of ytterbium oxides (A., 1922, ii, 463). It is contended that the difference between the observed wave-lengths and the theoretically calculated values is not outside the limits of possible error, that the lines cannot belong to higher orders of other elements, and that the line β_1 of celtium, lying between the two intense lines 1366·7 of lutecium and 1377·7 of copper, would not be expected to be visible on the photographic plate. G. F. M.

***L*-Series of Tungsten and Platinum.** J. S. ROGERS (*Proc. Camb. Phil. Soc.*, 1923, **21**, 430—433).—The values of the wave-lengths obtained for the *L*-series of tungsten and platinum are in good agreement with those given by Dauvillier and Coster, although there are discrepancies for some of the fainter lines. A number of new lines have been discovered, and ascribed to definite electron passages within the atom. In the tungsten spectrum, the line 1·4503 has been called α_3, and the line 1·2489, β_2', and the former

is ascribed to the passage $M_1 L_1$, and the latter to $N_3 L_1$. Other faint new lines have been observed. In the platinum spectrum, line 1·0660 has been called β_{10}, the line 1·0803 appears to be due to the passage from an O to a L_1 orbit, and the line 1·0375 may be due to the passage $M_1 L_3$. Calculations have been made of the energies of these lines, and good agreement is found with the calculated values. The lines fall on the Moseley graphs.

W. E. G.

Ultra-violet Absorption Spectra of the Cresols. F. W. Klingstedt (*Compt. rend.*, 1923, **176**, 674—676).—*o*-Cresol and *m*-cresol have almost the same absorption spectra, having two broad bands occupying approximately the same position as those of phenol at λ=2780 and 2716 for the former and at λ=2796 and 2720 for the latter. The coefficients of molecular absorption ϵ=1810 and 1770. Compared with toluene, the bands are considerably displaced towards the red, and their intensity is about nine times as great. *p*-Cresol has seven bands between λ=2858 and 2644. Compared with the *o*- and *m*-cresols, the spectrum of *p*-cresol is displaced 70 Å. towards the red, the intensity of absorption is greater, and, like other para-derivatives, there are numerous narrow bands instead of two wide bands, this distinction being so characteristic as definitely to identify a para-compound. The seven bands of *p*-cresol can be distributed into three groups, the difference in the frequencies of each group being constant, whilst the intensity of absorption decreases. The mean fundamental period, Δ_λ^1 =1217 Å.

G. F. M.

The Ethylene Chromophor. H. Ley and F. Rinke (*Ber.*, 1923, **56**, [*B*], 771—776; cf. Ley, A., 1917, i, 261; 1919, ii, 40).—A continuation of previous work.

The introduction of a methyl group into stilbene in the α-position causes a diminution of the selective absorption and a displacement of the continuous absorption towards the region of shorter wavelengths. The presence of a second methyl group increases the effect to such an extent that only a trace of selective absorption is observed with 7 : 7′-dimethylstilbene. A methyl radicle attached to the nucleus in the para-position has a normal influence. The spectroscopic analogy between stilbene and cinnamic acid is preserved in the methyl and dimethyl derivatives which contain the substituents in the aliphatic portion of the molecule.

The presence of a chlorine atom in the α-position of styrene has a weak, hyposochromic influence, whereas in the β-position it displaces the absorption towards greater wave-lengths. The absorption curve of 7-chlorostilbene is similar to that of the parent substance, with the exception that the band is sharper and somewhat displaced towards the ultra-violet; nuclear chlorine has a distinct bathochromic effect.

Comparison of the absorption curves of stilbene, 7-phenylstilbene, and 7 : 7′-diphenylstilbene shows that in the region of greater thicknesses or higher concentrations the absorption is progressively

displaced towards the red end, in the region of least transparency the absorption is diminished; with increase in the number of phenyl groups, the extinction coefficients become smaller, and the head of the bands is displaced slightly towards greater wave-lengths.

The additive compound of 7 : 7′-dimethylstilbene and 1 : 3 : 5-trinitrobenzene is markedly less coloured than the corresponding compound from 7-methylstilbene; similarly, in the phenylstilbene group the colour diminishes with increasing number of substituents.

βγ-Diphenyl-*n*-butane, m. p. 123—124°, is prepared by the action of magnesium on an ethereal solution of α-bromoethylbenzene; an isomeride, b. p. 162—164°/25 mm., appears to be produced simultaneously. Tetraphenylethylene, m. p. 221°, obtained from benzophenone chloride and sodium iodide in the presence of acetone, is reduced by sodium and boiling amyl alcohol to tetraphenylethane, m. p. 209°. α-Chlorostyrene has b. p. 83°/23 mm., 85—85·5°/22·5 mm., 73—74°/15 mm., d_4^{20} 1·0975, and 1·0916 for two different specimens. H. W.

Determination of Constitution by Spectrochemical Methods. The so-called Triphenylvinyl Alcohol. Enolic Salts. H. Ley and W. Manecke (*Ber.*, 1923, **56**, [*B*], 777—783).—As a result of purely chemical investigation, Meyer and Gottlieb-Billroth (A., 1921, i, 422) have been drawn to the conclusion that the so-called triphenylvinyl alcohol, CPh_2:CPh·OH, is actually a ketone, $CHPh_2$·COPh. Spectrochemical investigation leads the authors to the same conclusion.

The optical behaviour of "triphenylvinyl alcohol" is completely different from that of triphenylvinyl acetate, CPh_2:CPh·OAc, in which the enolic form is fixed. According to previous observations, it is to be expected that the optical properties of triphenylvinyl alcohol would not differ greatly from those of the parent hydrocarbon, 7-phenylstilbene; it is observed, however, that the absorption spectra of the hydrocarbon and triphenylvinyl acetate are closely similar, and differ entirely from that of triphenylvinyl alcohol. The enolic constitution of the latter compound is therefore regarded as impossible. Its ketonic nature is demonstrated by a comparison of its optical properties with those of acetophenone, deoxybenzoin, and β-benzpinacolin, COPh·CPh_3. Further, the colour of the additive product of "triphenylvinyl alcohol" and 1 : 3 : 5-trinitrobenzene shows that it is not a derivative of stilbene.

The optical behaviour of 9-benzoylfluorene, $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>$CHBz, has been examined in connexion with that of triphenylethanone. The parent hydrocarbon, 9-benzylidenefluorene, is closely analogous to 7-phenylstilbene, but the analogy between triphenylethanone and 9-benzoylfluorene is not at first sight so marked, probably by reason of the increased absorption attributable to the fluorenone ring. The absorption of the sodio-derivative of the enolic form of 9-benzoylfluorene has also been measured as well as that of the free enol (the apparatus required for the latter purpose is described in detail).

The enols, which have been generally investigated spectroscopically, contain a carbonyl group, and it has been assumed that in their salts the metal is also united to this group by a subsidiary valency, whereby an internal complex salt is produced. The authors consider this hypothesis untenable, and prefer to attribute the behaviour of the salts to the presence in them of readily altered, conjugated systems. H. W.

Mode of Absorption of Triphenylmethane Colouring Matters. E. ADINOLFI (*Atti R. Accad. Lincei*, 1922, [v], **31**, ii, 551—554).—Consideration of the various theories advanced to establish chemico-physical connexions between constitution and absorption, together with the results previously obtained (A., 1922, ii, 601), shows that triphenylmethane colouring matters, in solution in water or in methyl, ethyl, *iso*butyl, or amyl alcohol, give rise to absorption spectra of similar type, and with maxima which undergo increasing displacement as the molecular weight of the solvent increases. To this rule, rhodamine-*B* and uranine form exceptions, probably owing to re-emission resulting from fluorescence. The two characteristic absorption bands of these colouring matters are due to two distinct vibrators, which in some cases diffuse with unequal velocities, and in others disappear alternately in acid or alkaline solutions, and undergo displacements to different extents in different solvents. T. H. P.

Infra-red Spectroscopy. V. P. LUBOVICH and (MISS) E. M. PEAREN (*Trans. Roy. Soc. Canada*, 1922, **16**, III, 195—212).—The absorption of infra-red radiation by dilute alcoholic solutions of dicyanin, dicyanin-A, pinacyanol, nigrosin-SS, alizarin-blue-S, and Eastman red sensitiser No. 700 has been investigated. The results indicate that photography of the infra-red spectrum can be readily extended to λ 20,000 Å. Nigrosin and alizarin-blue are more suitable for the photography of certain regions of the spectrum than dicyanin or dicyanin-A. The infra-red spectra of tin, lead, bismuth, zinc, and antimony have been investigated from λ 8000 Å. to λ 11,000 Å. Particulars are given of the application of the "thalofide cell" to determine wave-lengths in infra-red spectra. J. S. G. T.

A Simple Appliance for Detecting Traces of Fluorescent Substances. ED. MOREAU (*J. Pharm. Chim.*, 1923, [vii], **27**, 184—187).—A box lined with black paper measuring about 8 cm. cube has a narrow observation slit in the middle of one side and a hole in the top opposite to the slit just large enough to take the test-tube containing the solution to be examined. This is illuminated from above by an electric lamp which is shaded from the observer by means of a cylinder fixed to the top of the box. By means of this appliance the least traces of fluorescence can with certainty be detected, and minute quantities of urobilin in biological work, fluorescein for detecting infiltrations in sanitary investigations, etc., can with certainty be found. G. F. M.

Destruction of the Fluorescence of Dilute Solutions by Ultra-violet Light. (MISS) F. M. CALE (*Trans. Roy. Soc. Canada*, 1922, **16**, III, 257—263).—Determinations have been made of the decrease of fluorescence of a dilute aqueous solution of æsculin by exposure to ultra-violet light. After the solution was once exposed, its fluorescence continued to decay even when the solution was kept in absolute darkness. On subsequent exposure of the solution to ultra-violet light, the rate of decay decreased very rapidly at first, then steadily. On further exposure, after an interval of several hours, the rate of decay was greater than before the interval. Ozone bubbled through the solution caused a very rapid decay of the fluorescence, the solution finally possessing the same colour and absorption spectrum as that transformed by ultra-violet light. J. S. G. T.

Tesla-luminescence Spectra. I. The Form of Apparatus and the Spectrum of Benzene. WILLIAM HAMILTON MCVICKER, JOSEPH KENNETH MARSH, and ALFRED WALTER STEWART (T., 1923, **123**, 642—654).

Luminescence of Compounds formed by the Action of Magnesium on *p*-Dibromobenzene and Related Compounds. W. V. EVANS and R. T. DUFFORD (*J. Amer. Chem. Soc.*, 1923, **45**, 278—285).—Solutions of magnesium *p*-bromophenyl bromide in ether are strongly chemi-luminescent, so much so that if it is dropped from a rod through air the luminescence is visible in daylight; stirring the solution in air gives a strong luminescence, and when poured from a tube it glows with a greenish-blue light which suggests molten metal. The luminescence of this substance has been compared with that of other aromatic halogen compounds, when the substances are exposed to air or oxygen. No luminescence results from the action of other gases, such as carbon dioxide, hydrogen sulphide, sulphur dioxide, and nitrogen on Grignard compounds. The spectrum of the chemi-luminescence of magnesium *p*-bromophenyl bromide has been investigated by the use of light filters, and its lower and upper limits have been found to lie within the region λ 5200—λ 3500. This spectrum is found to be distinct from that of the associated fluorescence spectrum. Photographs of two kinds of fluorescence have been obtained from the oxidation products, one giving a single-banded spectrum, the other an entirely different multiple-banded spectrum. J. F. S.

Spectral Study of the Triboluminescence of certain Substances. HENRI LONGCHAMBON (*Compt. rend.*, 1923, **176**, 691—693; cf. A., 1922, ii, 603).—A spectral study was made of the triboluminescence of tartaric acid, cadmium sulphate, uranium nitrate, and calcium fluoride. In spite of their widely different chemical constitution and crystalline form, the spectrum of the triboluminescence was in all cases the line spectrum of nitrogen. In the case of the uranium salt, however, and it would probably be so with other fluorescent substances such as the platinocyanides, etc., the triboluminescence was masked by the secondary pheno-

menon of fluorescence. Nevertheless, by the spectrographic method after an exposure of six hours, the presence of four other lines, coincident with the four most intense nitrogen lines, was revealed.

G. F. M.

Investigations on the Dependence of Rotatory Power on Chemical Constitution. XIX. The Rotatory and Refractive Dispersions and the Absorption Spectrum of *d*-γ-Nonyl Nitrite. ROBERT HOWSON PICKARD and HAROLD HUNTER (T., 1923, **123**, 434—444).

Rotatory Dispersion of the Esters of Lactic Acid. I. Normal Esters. CHARLES EDMUND WOOD, JOHN EDWARD SUCH, and FRANK SCARF (T., 1923, **123**, 600—616).

Magnetic Rotatory Dispersion in Gases. T. H. HAVELOCK (*Phil. Mag.*, 1923, [vi], **45**, 560—576).—A comparison is made between the ordinary dispersion of certain gases and the dispersion of magnetic rotation in regions free from absorption. The formulæ derived from a simple static molecule with one type of vibrator are sufficient for both dispersions in the visible spectrum for gases like hydrogen and nitrogen. In the case of oxygen, it is necessary to include the magnetic properties of the molecule before a complete theory can be formed. Omitting paramagnetic effects, expressions for the rotatory dispersion are obtained for the anisotropic static molecule, such as have been used for the ordinary dispersion of hydrogen. The Bohr molecule of hydrogen is studied numerically. In order that the adjustable constants of the ordinary dispersion formulæ may be known more accurately, it is desirable that parallel sets of observations on ordinary rotatory dispersion be made on the same gas under similar conditions. W. E. G.

The Mechanism of Photochemical Processes. II. The Behaviour of a Dry Mixture of Oxygen and Hydrogen. ALFRED COEHN and HEINRICH TRAMM (*Ber.*, 1923, **56**, [*B*], 455—458).—A repetition of Baker's work (T., 1902, **81**, 4000) has confirmed the observation that mixtures of hydrogen and oxygen which have been desiccated by prolonged contact with phosphoric oxide can be heated to redness in Jena glass tubes without the occurrence of an explosion. On the other hand, the presence of moisture does not appear to exert an appreciable influence on the rate of combination of hydrogen and oxygen when exposed to the ultra-violet light of the Heraeus lamp. Similar observations have been made previously (A., 1921, ii, 476) with mixtures of carbon monoxide and oxygen. H. W.

The Mechanism of Photochemical Processes. III. The Effect of Desiccation on the Combination of Hydrogen and Chlorine. ALFRED COEHN and HEINRICH TRAMM (*Ber.*, 1923, **56**, [*B*], 458—462).—The chlorine is dried and purified by fractional distillation at the temperature of liquid air. The hydrogen is prepared electrolytically, passed over heated palladised asbestos, and thence at increasing pressure through a series of U-tubes, in

each of which it is subjected to protracted cooling by liquid air. The moist and dry mixtures are exposed in quartz tubes to the light of a 100 candle-power Osram lamp; the gases are subsequently treated with neutral potassium iodide solution, and the liberated iodine and the hydrogen chloride estimated. Under identical conditions, the union of hydrogen with chlorine in the presence of moisture occurs quantitatively within twelve minutes, whereas in the dry mixture there is no sign of combination after two hours.

It has been shown previously (Coehn and Wassiljewa, A., 1909, ii, 846; Coehn and Stackardt, A., 1917, ii, 5) that hydrogen chloride, bromide, and iodide are decomposed to some extent by exposure to ultra-violet light. The presence of moisture is found to be without influence on the rate of decomposition of hydrogen bromide or iodide, whereas in the case of hydrogen chloride decomposition of the completely dry gas is not observed.

The velocity of combination of carbon monoxide with chlorine can be greatly reduced by thorough desiccation of the gases, but the process invariably takes place at an appreciable rate. Reaction in the case of sulphur dioxide and chlorine is completely inhibited by protracted drying of the gases. H. W.

The Mechanism of Photochemical Processes. IV. The Behaviour of Dry Mixtures of Hydrogen and Chlorine in Ultra-violet Light. ALFRED COEHN and GERHARD JUNG (*Ber.*, 1923, 56, [*B*], 696—698).—It has been shown recently (preceding abstract) that dry hydrogen and chlorine do not combine with one another when exposed to visible light. Under similar conditions, union is quantitative within twelve minutes under the influence of ultra-violet light; the wave-length of the active rays is less than 254 $\mu\mu$. H. W.

Spectrophoto-electrical Sensitivity of Bournonite and Pyrargyrite. W. W. COBLENTZ and J. F. ECKFORD (*U.S. Bureau of Standards Sci. Paper* No. 451, 1922).—A study of the effect of chemical constitution on spectrophoto-electrical sensitivity. The minerals were tested in the spectral region from 0·3 μ in the ultra-violet to 2 μ in the infra-red. Bournonite, $3(Cu_2Pb)S,Sb_2S_3$, has a high spectrophoto-electrical sensitivity from the extreme violet to 1 μ in the ultra-red with two wide, ill-defined maxima in the region of 0·55 μ and 0·95 μ, its reaction being entirely different from that of the constituent sulphides. The intrinsic intensity is greatly increased with fall of temperature, the maxima shifting towards the short wave-lengths. The spectrophoto-electrical reaction of pyrargyrite, Ag_3SbS_3, consists at 22° of a wide, unsymmetrical maximum in the ultra-violet with a weak, ill-defined maximum in the region of 0·63 μ. It also differs from that of the constituent sulphides, but resembles that of proustite (silver arsenic sulphide). At −165°, pyrargyrite reacts electrically to all wave-lengths from the extreme ultra-violet to 1·5 μ, but the greatest reaction is localised in the band at 0·63 μ. On increasing the intensity of the radiation stimulus, there is a more rapid increase

of the response of bournonite and pyrargyrite in the long wave-lengths than the short. In a general way, the properties of photo-electrical reaction spectra and absorption spectra are affected analogously by chemical constitution, indicating that the two phenomena may have a common source within the molecule.

T. H. B.

The Distribution of the Length of α-Rays. (MLLE) IRÈNE CURIE (*Compt. rend.*, 1923, **176**, 434—437).—A study of the distribution of the length of rays by photographing the trajectories obtained in an apparatus similar to that described by Wilson (A., 1913, ii, 92). On account of the difficulty of knowing in a precise manner the density of the gas in the chamber at the moment when the rays are emitted, the measurements are essentially a comparison of the length of the rays emitted at the same instant in an exposure. The rays used were those of polonium. For each exposure two curves are traced, namely, the number, n, of rays the lengths of which are comprised between $x-\Delta x$ and $x+\Delta x$, and the number, N, of rays of length superior to x in function of x. The first curve shows the existence of the most probable trajectory, l, of the rays. The second curve, the fall of which resembles that of Bragg's curve, shows that it is possible to define an extrapolated trajectory, p, in the same manner as Henderson defines it for the ionisation curve (A., 1921, ii, 617). Several hundred rays were photographed and curves are given for the results of 142 rays. The ratio of $p' : p$ for the rays of polonium and radium-C is exactly equal to that given by Geiger from the ionisation curve, namely, $6{\cdot}971 : 3{\cdot}925 = 1{\cdot}775$ (*Z. Physik*, 1922, 45). Except for the very short rays the results as plotted correspond exactly with a law of probability of the form $Ke^{-k^2x^2}$. About 90% of the rays have a length between $l-1$ and $l+1$ mm. The second curve shows that $p=l+0{\cdot}7$ mm., and taking for p the value 3·92 mm. as given by Geiger (*loc. cit.*) the most probable length of the trajectory will be 3·85 mm. in air at 15° and 760 mm. As a corollary, it is necessary to admit that the ionising power of an α-ray along its trajectory commences by increasing, passes a maximum 4—3 mm. from its end and then decreases rapidly during the last millimetres.

W. G.

Extension of the X-Ray into the Ultra-violet Spectrum. OTTO STUHLMAN, jun. (*Science*, 1922, **56**, 344).—When thermions liberated from a tungsten filament are accelerated and allowed to impinge on a metal grid maintained at a variable positive potential, secondary electrons are emitted from the grid, the number being measured by means of a galvanometer in series with the grid and a plate maintained at a constant positive saturation potential. When the secondary current is plotted as a function of the accelerating voltage, a sudden change in the slope of the curve occurs at critical potentials, the equivalent wave-lengths being calculated from the energy-quantum relation $V(\text{volts})L(\text{Å.})=12320$. Preliminary measurements are given in the case of tungsten and iron.

A. A. E.

The Increase of the Dispersion in the Photo-electric Spectra of X-Rays. RENÉ LEDRUS (*Compt. rend.*, 1923, **176**, 383—385).—The dispersion is best increased by exciting the electronic emission by means of an *X*-radiation, the frequency of which is slightly superior to the frequencies of the layers to be studied, and by adjusting the magnetic field so as to bring the regions studied towards the edge of the photographic plate which corresponds with high values of the radius of trajectory of the electron. These conditions have been fulfilled in a study of the spectrum of velocities of electrons emitted by a radiation of gold excited by the radiation from a molybdenum anti-cathode. Seven rays were observed and the results obtained agree closely with those calculated. W. G.

The Colson-Russell Effect, Photechie, Radiation from Metals, Photoactivity, and Other Similar Radiation Phenomena. E. RUMPF (*Jahrb. Radioaktiv. Elektronik*, 1923, **19**, 214—222).—A historical survey is given of the literature on this subject. The activity of a zinc surface has been investigated with a view to testing if the darkening of a photographic film is due to radiation or to the emission of corpuscles. Contrary to the observations of Blaas and Czermak (*Physikal. Z.*, 1904, **5**, 363), the colour of the gelatin film is without effect. The action on the photographic film is not stopped by 16 sheets of aluminium foil. Since the foil is pierced by numbers of small holes, the possibility of diffusion of gases from the zinc plate to the film has not been eliminated. A powerful stream of air over the surface of the zinc was effective, however, in preventing any darkening of the film, and by maintaining a potential difference of 150 volts between the film and the zinc plate, it was shown that the effect cannot be due to electrically charged corpuscles. The only explanation of the phenomenon would thus appear to lie in some chemical influence, such as that suggested by Russell, who ascribed the action to hydrogen peroxide formed during the oxidation of the zinc plate in the presence of water vapour. W. E. G.

Positive Rays in Simple Gases. J. J. McHENRY (*Phil. Mag.*, 1923, [vi], **45**, 433—443).—A study of the proportion of atomic and molecular positive rays of the simple gases under varying conditions of pressure in the discharge tube. The presence of mercury vapour in oxygen gas causes most of the positive rays to become atomic, and its removal always brings into prominence the molecular positive rays. Mercury seems to exert no effect on the nitrogen positive rays. The slower positive rays are mostly atomic, whilst those of greater energy are mostly molecular. Since the energy of a positive ray depends on the potential difference through which it falls to the cathode, those of small energy must be produced near the cathode. In this region ionisation by the cathode rays is at a minimum, and ionisation by positive rays at a maximum, so it would appear that the positive rays tend to give atomic ions, and cathode rays molecular ions. This view is in agreement with experiments made on the action of a magnetic field at varying distances from the cathode, in which it is shown

that the molecular positive rays are reduced in increasing measure as the distance from the cathode increases. The ratio of molecular to atomic positive rays is the greater the lower the pressure and the higher the voltage of the tube. In mixtures of one volume of hydrogen and two volumes of oxygen, the hydrogen positive rays are smaller in number than the atomic positive rays, but the ratios O_1/O_2 and H_1/H_2 are practically the same in the two cases. This regularity does not persist with other mixtures of hydrogen and oxygen. Carbon monoxide is more easily broken down into its atoms than oxygen, and the proportion of atomic positive rays is much greater in the former gas than in pure oxygen.

W. E. G.

The Radiation and Ionisation Potentials of the Rare Gases, and the Singlet and Enhanced Series of Argon. W. M. Hicks (*Phil. Mag.*, 1923, [vi], **45**, 480—496).—The true radiation and ionisation potentials are defined as the potentials required to produce radiation or ionisation of the atom when this is in its radiating configuration. The observed ionisation potential should be the sum of the dissociation potential and the true ionisation potential. In hydrogen, both radiation and ionisation potentials are observed, on account of the long life of the hydrogen atom. In the rare gases, the observed potentials are too large to represent the true values, although these gases are already in the atomic state. It is suggested that the ordinary atom in these gases is not capable of ionisation, but requires preliminary work to change it into a configuration capable of emission. The nature of these prepared atoms is discussed, and the true radiation and ionisation potentials deduced from the spectral lines of these gases. Evidence is adduced from the work of Kammenstine (*Astrophys. J.*, 1922, **55**, 343) as to the existence of prepared atoms of the rare gases with long life periods. The life of a prepared helium atom must be of the order 1/200 of a second, since a frequency of 220 cycles per second is just sufficient to enable an arc to strike in helium at 4 volts. Helium gives two types of prepared atoms, the first requiring about 1 volt less than the second for their preparation and possessing the longer life. The two forms are represented by · ● — · ●, and ● · — · ●, where a large dot represents an electron, a small dot a potential level, and a dash the nucleus. The true radiation and ionisation potentials of helium are given as follows: radiation potentials, He=1·14; He^+=7·4; ionisation potentials, He=4·75; He^+=13·5 volts. The ionisation and radiation potentials of neon may be explained, if there are three kinds of prepared atoms for this gas. The work required to change the first prepared state to the second is 6·1 volts, and to change the latter into the third is 11·8 volts. A similar analysis is made for argon from the work of Horton and Davies on radiation and ionisation potentials of argon, and from its spectrum. W. E. G.

Luminous Discharge in Iodine. Determination of the Ionisation Potential of Iodine. W. Albert Noyes, jun. (*J. Amer. Chem. Soc.*, 1923, **45**, 337—342).—The theory of the luminous

discharge put forward by Gibson and Noyes (A., 1921, ii, 610; 1922, ii, 812) has been discussed with reference to its applicability to the luminous discharge in an electro-negative gas or vapour such as iodine vapour. The discharge potential in iodine vapour at various temperatures between $-3°$ and $29°$ has been determined. From the experimental values the most probable value of the ionisation potential of iodine is found to be $10{\cdot}0 \pm 0{\cdot}2$ volts. This leads to the value 8·4 volts as the ionisation potential of the iodine atom which would correspond with a wave-length of 1472 Å. It is impossible to verify this from the spectrographic data now available.

J. F. S.

Liquid Chlorine as an Ionising Solvent. J. Mennie and D. McIntosh (*Trans. Roy. Soc. Canada*, 1922, **16**, III, 301—305).—In agreement with the observations of Johnson and McIntosh (A., 1909, ii, 881), the authors find no evidence of ionisation when inorganic substances or ordinary organic compounds are dissolved in liquid chlorine. Ethyl ether, ethyl alcohol, acetone, and ethyl acetate dissolved in liquid chlorine yield conducting solutions when hydrochloric acid is added, and determinations are detailed of the variations of the conductivities of these solutions as the amount of acid is increased up to 2·5 molecular proportions. In the case of alcohol, the conduction is due to the ionisation of an oxonium acid compound by the acid. The results obtained with a solution of acetone in toluene, to which hydrochloric acid was added, resembled those for the corresponding liquid chlorine solution, but the actual conductivities were much smaller in the former case.

J. S. G. T.

Condition of Bismuth Salts in Aqueous Solutions and the Molecular Electrode Potential of Bismuth. David F. Smith (*J. Amer. Chem. Soc.*, 1923, **45**, 360—370).—The electrical conductivity and solubility of bismuth nitrate have been determined in solutions of nitric acid containing various quantities of acid at 25°. The results indicate that bismuth nitrate exists in solutions containing a considerable excess of nitric acid mainly in the form of partly ionised normal salt. Conductivity measurements of solutions of bismuth perchlorate show that the very soluble basic salt, $Bi(OH)_2ClO_4$, has the conductivity of a non-hydrolysed uni-univalent salt like potassium nitrate, and that it is converted into less basic salts such as $Bi(OH)(ClO_4)_2$ and $Bi(ClO_4)_3$ only slowly on the addition of an excess of acid. Even when the ratio of perchlorate to bismuth is as much as 4 : 1, not more than 40—50% of the bismuth oxyperchlorate is converted into the hydroxy-salt, $Bi(OH)(ClO_4)_2$. *E.M.F.* measurements of cells of the type $H_2|HClO_4||HClO_4+BiOClO_4|Bi$ have been made at 25° for various concentrations of perchloric acid and the bismuth salt. The results fully confirm the conclusions drawn from the conductivity values. The measurements lead to the following values for the molecular electrode potential of bismuth, which were calculated on the two assumptions that the bismuth in solution exists entirely as the ion BiO^+ and the ion $Bi(OH)^{++}$, respectively: $Bi|BiO^+ + H^+$:

-0.314 volt, $Bi|Bi(OH)^{++}+H^{+}$: -0.298 volt. For comparative purposes, the electrical conductivity of solutions of nitric and perchloric acid have also been measured at 25°. J. F. S.

Electrode Potential of Bismuth determined by Equilibrium Measurements. ERNEST H. SWIFT (*J. Amer. Chem. Soc.*, 1923, 45, 371—377; cf. preceding abstract).—The position of the equilibrium between bismuth and copper perchlorates and metallic copper and bismuth has been determined at 25° by shaking together the metal and the perchlorate of the other metal and analysing the equilibrium mixture. The reaction is represented by the equation $3Cu + 2Bi(ClO_4)_3 \rightleftharpoons 2Bi + 3Cu(ClO_4)_2$, and from the composition of the equilibrium solution the value of the molecular electrode potential of bismuth has been calculated on the assumption that the bismuth exists in such solutions entirely as the ion $BiO^{\cdot}$ and on the assumption that it exists solely as the ion $Bi(OH)^{\cdot\cdot}$ and that the free perchloric acid present is completely ionised. The following values, referred to the molecular hydrogen electrode, were obtained: $Bi|BiO^{\cdot}+H^{\cdot}\|=-0.318$ volt, $Bi|Bi(OH)^{\cdot\cdot}+H^{\cdot}\|=-0.310$ volt. If the copper salt is regarded as completely ionised, whereby the errors in the ionisation assumptions are partly compensated, there result values which differ by about 5 m.-volt from the above, namely -0.323 and -0.314 volt, respectively. These results are in fair agreement with the values -0.314 and -0.298 volt obtained by Smith (*loc. cit.*) from *E.M.F.* measurements. J. F. S.

Hydrogen-Chlorine Cell. F. FOERSTER [with A. NOBIS, and H. STÖTZER] (*Z. Elektrochem.*, 1923, 29, 64—79).—With the object of finding a method by which chlorine and hydrogen can be combined on the large scale to form hydrochloric acid, the authors have investigated the element $Pt,H_2|HCl|Cl_2,Pt$. The cell was built up in a U-tube which was divided at the bend by a porous diaphragm, platinised electrodes were inserted and chlorine was led into one side, hydrogen into the other. It is shown that with such an arrangement current is furnished without any great amount of polarisation up to 10^{-2} amperes/cm.^{2} of platinum surface in the solution. The action consists in the combination of hydrogen and chlorine to form hydrogen chloride, and since the transport number of the hydrogen-ion is greater than that of the chloride-ion, the concentration of the hydrochloric acid in the chlorine side of the cell increases much more rapidly than in the hydrogen side. By increasing the temperature, the terminal voltage of the cell increases up to a definite maximum temperature which is higher the larger the current drawn from the cell. At 80°, however, the voltage falls when large currents are drawn from the cell, because the reduction in the gas concentration retards the electromotive action more than it would normally have been increased by the increase in temperature. The velocity of the electromotive action of the chlorine is very great and independent of the nature of the electrode, platinum or various forms of carbon being equally good. Hydrogen, however, requires the catalytic action of platinum black to give it a somewhat larger activity, and even when this is used the

reaction velocity of the hydrogen is not very large, so that a marked polarisation appears when considerable quantities of current are withdrawn. The electromotive activity of the hydrogen is restricted to the thin layer of the electrolyte covering the surface of the electrode which protrudes into the gas atmosphere. To increase the surface layer and to keep the concentration of hydrogen in it sufficiently high to furnish the necessary amount of current, it is essential that a very rapid stream of hydrogen should be passed into the solution. Platinised carbon will serve as electrode just as well as platinised platinum. The action is very slow if a bright platinum electrode is used, and it does not take place at all with carbon electrodes. In apparent connexion with this is the fact that the overvoltage of hydrogen on carbon electrodes is considerable. On paraffined carbon electrodes the overvoltage of hydrogen shows unexpectedly large variations with time. Combinations such as H_2|carbon|HCl|carbon|Cl_2 or H_2|bright Pt|HCl|carbon|Cl_2 give *E.M.F.* values which arise from concentration cells of the form Cl_2(of small partial pressure)|HCl|Cl_2(p=1 atm.). If on a platinised electrode the process $H_2 \rightarrow 2H^{\cdot}+2\ominus$ is no longer sufficient to furnish the current, the electrode becomes polarised to +0·8—+0·9 volt, and the current furnishing process is then $Pt \rightarrow Pt^{\cdot\cdot\cdot\cdot}+4\ominus$, which continues as long as the platinum deposit lasts. The potential of the element Pt|0·01$M$$H_2PtCl_6$ in 2NHCl|| has been measured and found to have the value +0·74 volt. Oxygen is capable, if but slowly, of displaying an electromotive activity on carbon electrodes, which appears to be brought about by a small quantity of a carbon oxide present on the electrode. By using comb-shaped electrodes, of which the one in the hydrogen part of the cell is platinised, cells of about 600 c.c. capacity can be constructed which will furnish a continuous current of 0·5—0·63 ampere at 0·75 volt for many hours. To achieve this result, the hydrogen must be led in at 10—30 litres per hour. In the chlorine part of the cell 10N-hydrochloric acid is produced with a 90% yield calculated on the chlorine led in, and a material yield on the hydrogen of 1—2%. In view of the necessity of using highly platinised electrodes and a very high rate of flow of hydrogen, it is shown that the process considered is impossible for the commercial manufacture of hydrochloric acid. The burning of hydrogen in chlorine is a more suitable and at the same time a simpler process for this purpose. J. F. S.

New Form of Electrical Resistance of Electrolytes. MAURICE PHILIPPSON (*Bull. Acad. roy. Belg.*, 1922, [v], 8, 76—80).—Since an electrolytic ion possesses inertia, the magnitude of an alternating current passing through an electrolyte should decrease as the frequency of the current increases, the effect being analogous to that of electromagnetic self-induction. An electrolyte should, in fact, possess two kinds of resistance, frictional and kinetic. The author obtained evidence of the existence of the latter kind of resistance and succeeded in measuring the "self-inductance" and "kinetic reactance" of an electrolytic cell,

using a resonance method, "tuning" a circuit containing the cell to one in which induced alternating currents of known frequency were produced. For a cell of 20 ohms resistance, containing a normal solution of potassium chloride, the kinetic reactances corresponding with frequencies of 4×10^5, $1{\cdot}5\times10^6$, and 3×10^6, were found to be respectively 0·60, 13·09, and 7·35 ohms, a maximum figure also being obtained at frequency $1{\cdot}5\times10^6$ when a cell of 100 ohms resistance was used, or when sodium lactate or acetate was substituted for potassium chloride. For frequencies of 1×10^6 to 3×10^6, the kinetic reactance of a cell is roughly proportional to the volume of solution between the electrodes. E. E. T.

Anodic Behaviour of Metals in Non-aqueous Solutions. III. Iron, Nickel, Cobalt, and Chromium in Ethyl-alcoholic Solutions of Nitrates. UMBERTO SBORGI and GINO CAPPON (*Nuovo Cim.*, 1922, [vi], **23**, 303—331).—The authors have investigated the anodic behaviour of various metals in ethyl-alcoholic solutions of calcium and ammonium nitrates, the apparatus employed being similar to that previously used (A., 1921, ii, 572), but modified to render it applicable at higher temperatures and to allow of the separate collection of the anodic and cathodic gases.

Cobalt exhibits complete activity, dissolving as a bivalent metal at all current densities from 0·03 to 3 amps. per sq. dcm., and at all temperatures (from −10° to 60°). The other three metals show passivity phenomena. Nickel is passive at all temperatures from −10° to 25°. At 60°, it is partly active if the current-density is high (0·3—3 amps. per sq. dcm.); in the ammonium nitrate solution, at low current density (0·03), not only is there complete electrochemical activity, but superposed on this is chemical activity, nickel being attacked by alcoholic ammonium nitrate, particularly at high temperatures. With iron, there is complete passivity at all temperatures and current densities employed.

Chromium shows in the alcoholic solutions passivity phenomena similar to those observed in aqueous solutions, the attack being approximately (but somewhat less than) sexavalent; chromic, and not chromate, ions appear.

In the alcoholic calcium nitrate solutions, there is formed at the cathode a badly conducting layer composed, partly at least, of calcium ethoxide. In all cases in which partial or total passivity is observed at 25°, oxygen is liberated at the anode in amount corresponding with 7·5% of the total current, the remainder, allowing for the current expended in dissolving the metal, giving rise to acetaldehyde; the latter is formed almost quantitatively, only a trace of acetic acid being obtained. T. H. P.

Application of the Theory of Magnetism to the Calculation of Atomic Diameters. J. F. T. YOUNG (*Trans. Roy. Soc. Canada*, 1922, III, **16**, 49—61).—Attention is directed to the periodic distribution of paramagnetic and diamagnetic properties among the elements arranged in the customary periodic table. A mathematical theory, applicable either to the dynamic or static atomic model, permitting atomic dimensions of an element to be calculated

from the value of the magnetic permeability is detailed, and the results are applied to calculate the atomic radii of 26 elements. The values obtained are of the correct order in all cases.

J. S. G. T.

The Specific Heat of Saturated Benzene Vapour, and the Adiabatic Curve of the Liquid-Vapour Mixture. G. BRUHAT and A. DELAYGUE (*J. Phys. Radium*, 1923, 4, 1—10).—From the experimental critical constants of benzene, its specific heat at low pressure, and its heat of evaporation, deductions have been made of the specific heat of the saturated vapour over a range of temperatures. At low temperatures, and in the neighbourhood of the critical temperature, this specific heat is negative, but at intermediate temperatures becomes positive. The values deduced for the two inversion points, 121° and 254°, are in good agreement with the experimental values 122° and 258° (cf. A., 1922, ii, 348). From the specific heats of the saturated vapour, the entropies of the vapour, the liquid, and mixtures of both have been deduced for temperatures ranging from ordinary temperatures up to the critical temperature. On a diagram, in which values of the entropy are plotted against temperature, the paths of the points for which an adiabatic expansion does not change the relative amounts of the two phases is indicated. By employing Young's tables, the usual volume–temperature and pressure–temperature diagrams may be constructed.

W. E. G.

The Specific Heats of Nitrous and Nitric Oxides. J. R. PARTINGTON and W. G. SHILLING (*Phil. Mag.*, 1923, [vi], 45, 416—430).—The specific heats of nitrous and nitric oxides are of special interest from the point of view of the Lewis-Langmuir theory, because of the similarity of the electronic configurations of nitrous oxide and carbon dioxide, and of nitric oxide, carbon monoxide, and nitrogen. Nearly all the previous work on nitrous oxide was vitiated by the use of impure gas, and results varying from $C_p/C_v=1{\cdot}25$—$1{\cdot}32$ are recorded in the literature. For nitric oxide, previous values range from 1·38—1·415. The nitrous oxide in the present experiments was freed from oxygen and nitrogen by passing it through a tube immersed in liquid air. The ratio of the specific heats of the two gases was determined by measurement of the relative velocities of sound in these gases and in pure dry air. The effect of the tube on the velocity of sound was eliminated. It was shown that Wohl's equation of state has no advantage over that of Berthelot for the reduction of the results, and that of the latter is employed as the basis of the calculation of the specific heats. The values obtained were, for nitrous oxide, $C_p/C_v=1{\cdot}302$, $C_p=8{\cdot}799$ cal., $C_v=6{\cdot}758$ cal.; for nitric oxide, $C_p/C_v=1{\cdot}400$, $C_p=6{\cdot}990$ cal., and $C_v=4{\cdot}993$ cal.

W. E. G.

The Meaning of *a* and *b* in the Equation of State. ANGUS F. CORE (*Phil. Mag.*, 1923, 45, [vi], 622—624).—In the general virial equation, $pv=RT+B/v$, the term B/v does not naturally fall into two parts, one of which is proportional to the temperature,

RTb/v, and the other independent of the temperature *a/v*. It is necessary to define either *a* or *b*. Thus *a/v* may be defined as half the work necessary to abstract *N* molecules chosen at random from the interior of the gas to infinity outside the gas, the other molecules remaining fixed in position. Thus defined *a/v* corresponds most closely with the equation of van der Waals. The term *RTb/v* cannot be called the collision virial, for when the molecules contain a hard kernel it does not in general reduce to the collision virial of Reinganum. The effect of making *RTb/v* equal to the collision virial is critically discussed, and shown to lead to $a/v=0$ if the molecule is regarded as a hard sphere without external field. W. E. G.

Freezing Points of Organic Substances. VII. JEAN TIMMERMANS (*Bull. Soc. chim. Belg.*, 1922, **31**, 389—397; cf. A., 1921, ii, 622).—The freezing points of a further 68 organic liquids are given in tabular form. The results confirm the author's previous conclusion that the alternation of melting points between the odd and even members of a homologous series is a general phenomenon, and allow this generalisation to be extended to include substances possessing two hydrocarbon chains linked by a central characteristic group (secondary amines, ethers, alkyl sulphides, etc.). Inverse alternation, in which the odd members of a series melt at a higher temperature than the adjacent even members, is shown to be frequent, even in series of symmetrical compounds. The melting points of the higher terms of all the homologous series considered tend towards a common value of 117° and, further, for the paraffins and most of their monosubstitution derivatives, it is found that the C_{30} member melts at about 65°, the C_{16} member at about 20°, and the C_8 member at about −45°. Compounds containing an amino- or a hydroxyl-group do not conform to this rule, their melting points being always higher than those quoted above. Amongst the lower members of a series there is often considerable and irregular variation in the melting points of successive members, but a minimum is usually observed at about the C_3 term. H. H.

Outer Jacket for Beckmann's Boiling-point Apparatus. JAMES FREDERICK SPENCER (*J. Soc. Chem. Ind.*, 1923, **42**, 126).—An outer jacket for the Beckmann boiling-point apparatus is described. The jacket is made on the same plan as the usual porcelain jackets, but is of copper. The mica windows are carried by light copper castings brazed to the inner and outer walls of the jacket. Only one side tube is attached to the jacket and this serves for putting the solvent and beads into the jacket and also for carrying the condenser. The boiling tube is supported by a ring of cork placed at the top of inside wall of the jacket. The jacket is superior to porcelain and glass jackets since it reduces the breakage and danger of fire with inflammable liquids to a minimum, and since it is less sensitive to draughts the equilibrium temperature is reached more rapidly and becomes steady much more quickly. J. F. S.

Comparison of the Normal Boiling Temperatures of Undesiccated Sulphur as Measured by the Dynamic and Static Methods. ALAN W. C. MENZIES (*J. Amer. Chem. Soc.*, 1923, **45**, 327—331).—Since the boiling point of sulphur is used as a standard in thermometry, the author has redetermined this value by both the static and dynamic methods with the object of ascertaining whether or no the equilibrium between liquid sulphur freshly condensed from recently generated sulphur vapour and sulphur vapour occurs at the same temperature as that between liquid sulphur and vapour of a greater age, at the same pressure near to 760 mm. The results show that the boiling point of undesiccated sulphur is the same whether the dynamic or the static method be used. The actual values are not given in the paper, but it is stated that the two values do not differ by more than 0·02°, an amount which is not outside the estimated error of the experiment. It is suggested that this similarity might not be found if the sulphur were accidentally or intentionally intensively desiccated. The statement that delay may occur before a new phase, freshly formed, reaches its equilibrium constitution and properties, has been examined for certain cases of liquids and vapours. J. F. S.

A New Process of Microsublimation. RICHARD KEMPF (*Z. anal. Chem.*, 1923, **62**, 284—291).—The substance to be sublimed is placed on a square brass plate, 12 cm. square and 1 cm. thick, heated by means of two resistors of nickel-chromium wire connected with an external resistance and regulator. The resistors are so arranged that they may be used separately or together, either in series or in parallel. The layer of substance is made as thin as possible and is covered, at a distance of 0·1 to 0·01 mm., with the microscope slide. In this arrangement the temperature of the plate can be kept constant over long periods and by suitable cooling of the slide, sublimates of most substances in characteristic forms may be obtained at comparatively low temperatures, *e.g.*, for mercuric chloride 17°, arsenic and sulphur 50°, stearic acid 38°, vanillin 53°, indigotin 95°, cocaine 36°, strychnine 103°. These temperatures are considerably lower than those at which the substances sublime in a vacuum. By this process characteristic crystalline deposits from evaporated human urine and blood may be obtained, even if present as stains on fabrics, so that the method may find application in forensic analyses. A. R. P.

Heat of Oxidation of Glucinum. H. COPAUX and CH. PHILIPS (*Compt. rend.*, 1923, **176**, 579—580).—A redetermination of the heat of oxidation of glucinum by measuring separately the heat of dissolution of the metal and its oxide in acids, and taking into account this time the variation from unity of the specific heat of the acid solutions used, gave a value of 131·3 Cal. The heat of oxidation of calcium determined in a similar way as a check on the correctness of the principles employed was 150 Cal., a value in close agreement with that obtained by Guntz by other methods. G. F. M.

Heats of Combustion and Energy of Dissociation. III. A. VON WEINBERG (*Ber.*, 1923, **56**, [*B*], 463—466; cf. A., 1920, ii, 668—669).—A reply to Fajans (A., 1922, ii, 818) and to Hückel (A., 1922, ii, 818). H. W.

Calorimetric Researches. III. Some Remarks on an Attempt of Swientoslawski to Calculate the Heat of Combustion of Benzoic Acid by a Semi-theoretical Method. P. E. VERKADE (*Rec. trav. chim.*, 1923, **42**, 105—111; cf. A., 1922, ii, 474, 740).—A critical survey of the conclusions drawn by Swientoslawski and Popov (A., 1915, ii, 315) and of the method of calculation adopted. The author stresses his criticism on the ground that benzoic acid is accepted as the calorimetric standard substance with a heat of combustion of 6324 $cal._{15°}$ per g.(air), which is about 2% greater than the value given by Swientoslawski from a consideration of various experimental results (A., 1918, ii, 32; 1921, ii, 679). H. J. E.

The Calorific Value of Organic Substances. D. P. KONOVALOV (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 81—105).—The heats of combustion of many naturally occurring fuels and of many organic substances are compared. These heats are calculated, not on unit weight of substance burned, but as calories per unit quantity of oxygen used in the combustion. A new factor, π, the oxygen potential of carbon compounds, is introduced. This is calculated from the equation $\pi = T/K$, where T, the calorific power, is the heat of combustion, Q, minus the heat of vaporisation of the water produced, and K, the oxygen coefficient, is the ratio of the weight of oxygen used, to the sum of the weight of substance and of the water produced. π is calculated for a number of different coals, for petrol, for animal fat, and for various types of saturated aliphatic compounds, including paraffins, alcohols, amines, ketones, aldehydes, and acids, and found to vary very little for these substances, the mean value being 3·05 Cal., and hence π for normal carbon compounds is very little different from that for pure carbon. In the case of compounds containing oxygen, it is incorrect to calculate the heat of formation or combustion on the basis that one oxygen atom may be balanced against two hydrogen atoms in the compound; the correct method is to balance one carbon against two oxygen atoms. A formula for the calculation of the heat of formation of oxygen-containing saturated aliphatic substances is given, and the results obtained from it are found to agree satisfactorily with those found experimentally for a number of substances. In the case of nitro-compounds, however, in which the oxygen is united to nitrogen and not to carbon, this formula cannot be applied, and in these cases the heat of formation may be calculated by assuming that the oxygen is present in the free state. In the case of homologous hydrocarbons, it is found that π gradually increases as the proportion of hydrogen falls. Formulæ for the calculation of π for unsaturated hydrocarbons are deduced, and found to agree satisfactorily with results obtained experimentally for ethylene, acetylene, and allylene, π in these cases increasing with the degree

of unsaturation. The same formula is applied to the calculation of π for carbon as C_2, which is found to 4·704. From this result, the heat of vaporisation of C_2 is calculated to be 103·6 Cal. π for saturated cyclic compounds differs little from that for straight chains, whilst for aromatic compounds it increases with increasing unsaturation, varying between 3·1 for benzene and 3·138 for diphenylacetylene. For terpenes, this value is of the same order as for aromatic substances. For rings containing oxygen, however, a great increase is observable, π for ethylene oxide being 3·585, for furfuraldehyde 3·364, and for trioxymethylene 3·509. Esters, such as ethyl nitrite, glyceryl trinitrate, and mannitol hexanitrate, behave differently from ordinary nitro-compounds, liberating more energy on combustion. A formula is deduced for the calculation of the heat of combustion of such substances, and it is shown that results calculated from it agree well with experimental figures. For cyanogen, π is only slightly less than for C_2, *i.e.*, 4·097, whilst for hydrocyanic acid it is 3·847, both being very close to calculated values. Nitriles also give values for π above the normal, and a small increase is apparent for compounds in which every carbon atom has a hydroxyl group attached, such as glycerol. Acid amides and carbamide, on the other hand, have a value below normal, *e.g.*, for carbamide $\pi = 2·914$, and for oxamide 2·739. Many organic acids, such as acetic, propionic, malonic, and succinic acids, have also low values. Carbohydrates have all values considerably above normal, the heat effect being on the average 7·5% greater than that of their carbon content alone. Lignite and peat have slightly higher values than the normal, 3·05, although lower than that of cellulose, 3·262, indicating that they are transition stages to coal. R. T.

The Heats of Combustion and of Formation of certain Explosive Nitro-compounds from their Elements. P. P. Rubcov and L. A. Severjanov (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 140—144).—The heats of combustion of various nitro-compounds are measured and their heats of formation hence calculated. These are, for 1 : 3 : 5-trinitrobenzene 3178 cal. and + 8·5 Cal., respectively, for 2 : 4 : 6-trinitro-1-methylnitroaminobenzene 3016·5 cal. and − 14·2 Cal., for 2 : 4 : 6-trinitrotoluene 3691 cal. and + 13·6 Cal., for 2 : 3 : 4 : 6-tetranitro-1-methylnitroaminobenzene 2551 cal. and − 29·9 Cal., for ammonium picrate 2890 cal. and + 78 Cal., for the ammonium salt of hexanitrodiphenylamine 3128 cal. and + 14 Cal., and for trinitroethane 1777 cal. and + 4·3 Cal. R. T.

Nernst's Theorem. Th. de Donder (*Bull. Acad. roy. Belg.*, 1922, [v], 8, 461—465).—The author obtains various expressions for the heat of reaction at constant pressure, making use of Nernst's theorem. E. E. T.

Heat of Coagulation of Ferric Oxide Hydrosol with Sodium Sulphate. Frederick L. Browne (*J. Amer. Chem. Soc.*, 1923, **45**, 311—321).—The heat of coagulation of ferric oxide hydrosol,

of widely varying purity, by means of 0·2*N*-solution of sodium sulphate, has been investigated, using sols prepared by three dissimilar methods. The sols employed were prepared, by the oxidation of a solution of ferrous chloride with hydrogen peroxide followed by dialysis, by the peptisation of precipitated ferric hydroxide in ferric chloride solution, and by the addition of various amounts of hydrochloric acid to a sol of a high degree of purity prepared by the first-named method. The same value for the heat of coagulation at a given purity and total iron concentration is obtained with sols prepared by all three methods, indicating that ferric oxide hydrosols represent an equilibrium which is defined by the temperature, pressure, concentration, and purity. The change in the degree of dispersion of ferric oxide during coagulation does not involve a measurable heat effect. The heat effects observed during the coagulation of sols of low purity are due to the dilution of the ferric chloride and hydrochloric acid contained in the sols, to the mixing of these electrolytes with the added coagulating electrolyte, and to changes in the adsorption equilibria. J. F. S.

Interfacial Tension. James Robert Pound (T., 1923, **123**, 578—599).

Viscosity, Neutralisation, and Isomorphism. L. J. Simon (*Compt. rend.*, 1923, **176**, 437—440).—A study of the variation in viscosity of solutions of phosphoric acid and arsenic acid during their neutralisation by sodium hydroxide shows that the curves obtained for the two acids are superposable. The results indicate that, in aqueous solution, of the same molecular concentration, isomorphous substances modify the viscosity of water at a given temperature in the same manner. By isomorphous substances is meant those having similar chemical formulæ, the same crystalline form and showing syn-crystallisation. A study of the chlorides of sodium, potassium, rubidium, and ammonium shows that this holds good for the last three named, but that for sodium chloride there is a marked difference at all temperatures and all concentrations.

W. G.

Dissociation Pressures of certain Salt Hydrates by the Gas Current Saturation Method. Walter C. Schumb (*J. Amer. Chem. Soc.*, 1923, **45**, 342—354).—Measurements of the dissociation pressures of nine pairs of salt hydrates have been made by the gas current saturation method at 25°, and the results compared with those obtained by other investigators using the same or other methods. The pairs of hydrates examined were the mono- and di-hydrates of barium chloride, di- and hexa-hydrates of strontium chloride, tri- and penta-hydrates of copper sulphate, anhydrous sodium sulphate and the decahydrate, hexa- and hepta-hydrates of magnesium, zinc, ferrous, cobalt, and nickel sulphates. It is found, contrary to the experience of several who have previously used the method, in particular Menzies (A., 1920, ii, 738) and Baxter and Lansing (A., 1920, ii, 286), that when suitable precautions are taken perfectly trustworthy results are obtained.

The necessary precautions concern the size of the saturator containing the mixture of salt hydrates, the method of measuring the total internal pressure, the intimate mixing of the two solid phases, the rate of flow of the current of air passing through the apparatus, and the weighing of the water taken up by the air. It is shown that the objection raised to this method, namely, that insufficient time is given for the attainment of an equilibrium, is without foundation, since the equilibrium may be reached from both sides. No certain relationship has been found to hold between the composition of analogous salt hydrates and their dissociation pressures measured at a given temperature, although the influence of such factors as atomic volume and valency is admitted. Exception is taken to the generalisations of Clark and Buckner (A., 1922, ii, 300) connecting the composition of ammines and hydrates with their stability, in view of the numerous exceptions found in the literature. It is pointed out that much further work is necessary, both in the formation and examination of new molecular compounds and in showing that numerous assumed compounds have no real existence, before any definite relationships can be established. J. F. S.

Abnormal Osmosis through Collodion Membranes. G. Preuner [with O. Roder] (*Z. Elektrochem.*, 1923, **29**, 54—64).—A number of osmosis experiments with dilute solutions of various potassium salts are described together with measurements of the potential difference at the collodion walls used to separate the dilute from the more concentrated solutions. The osmosis is shown to reach a maximum value at concentrations between $N/256$ and $N/512$. It is shown that when a concentrated solution is separated from a dilute solution by a collodion membrane a fall of potential is brought about by the diffusion, and this drives the solvent from the dilute solution to the concentrated solution, and so brings about the abnormal osmosis. Since the diffusion potential between the walls of the membrane depends on the fall of concentration inside the walls of the membrane, it follows that the abnormal osmosis is different with rotating membranes than with fixed membranes. With fixed membranes and stationary solutions the concentration on the surface of the membrane contiguous with the dilute solution is much greater than that in other portions of this solution. The ratio of the concentration on the two walls of the membrane approaches a maximum with increasing concentration of the concentrated solution. The maximum is reached at a concentration such that with the same concentration on both sides of the collodion wall the electro-endosmosis and the electro-adsorption potential ζ also have their maximum value. This is explained if it be assumed that at this concentration the coefficient of diffusion is at its minimum. Such an assumption is in keeping with the fact that the diffusion potential difference is much greater with membranes than without. The electrolyte behaves in the membrane as though the migration velocity of the anion, v, is reduced, and the more reduced the greater the value of ζ. Since in the equation for the diffusion potential difference the value of $(u-v)/(u+v)$

and the ratio of the concentrations, for concentrations in the region where the more concentrated solution shows a maximum osmotic pressure, decrease in the same way as ζ, the maxima of the diffusion potential difference of the abnormal osmosis and the electro-endosomosis must lie close together. With rotating membranes, the concentrations on the surface of the membrane differ only slightly from the concentration in the interior of the solution, since there is only a fall of concentration over the very thin adhering layer of the solution on the outside of the membrane. The diffusion potential difference increases with increasing concentration of the concentrated solution up to a very high value of this concentration. For these reasons, and because of the increased pure osmotic action, no maximum of the transport of liquid occurs. The maximum of the abnormal osmosis with collodion membranes is due to a further cause, if, as is stated by Loeb, it is caused by the increase in the diffusion potential difference and the decrease in the charge on the membrane with increasing concentration of the more concentrated solution. J. F. S.

Potential Difference occurring in a Donnan Equilibrium and the Theory of Colloidal Behaviour. A. V. HILL (*Proc. Roy. Soc.*, 1923, [*A*], **102**, 705—710).—A theoretical paper in which the contention of Loeb (Proteins and the Theory of Colloidal Behaviour), that the Donnan membrane equilibrium (A., 1911, ii, 848) involving the presence of an ion which does not diffuse, is the basis of the colloidal properties of a protein solution, is discussed. Whilst the possibility of Loeb's conclusion is admitted, it is pointed out that one of the main arguments used in its favour by Loeb is incorrect. Loeb shows that the potential difference observed experimentally between a protein and a non-protein solution separated by a membrane agrees very exactly with that calculated from the difference in hydrogen-ion concentrations also observed experimentally, and concludes that this supports his hypothesis. As a matter of fact, this equality is a necessary and inevitable consequence of the manner in which the observations were made and of general thermodynamic principles, and its proof is independent of any hypothesis of the mechanism by which the potential difference is produced. J. F. S.

Anomalous Osmosis of Solutions of Electrolytes with Colloidal Membranes. I. The Electrical Properties of the Membrane System. F. E. BARTELL and DWIGHT C. CARPENTER (*J. Physical Chem.*, 1923, **27**, 101—116).—It is shown that in the measurement of osmosis in collodion bags as prepared by Loeb (A., 1919, ii, 399, 497) an increase in volume of 15% is brought about by small heads of solution which causes a considerable error in the pressure values obtained. To avoid this source of error, the authors have used collodion membranes prepared by Bigelow and Gemberling's method (A., 1907, ii, 933), which they find are uniform in thickness and permeability, and by regulating the conditions under which they are formed the permeability can be adjusted to any particular value. The membranes were mounted in a non-

leaking osmotic cell made of two T-shaped glass compartments of equal volume, held together by a brass coupling which holds the membrane firmly between the two compartments. The osmosis values of 1·0, 0·1, 0·01, and 0·001M solutions of hydrochloric acid and potassium hydroxide, chloride, sulphate, ferrocyanide, ferricyanide, carbonate, phosphate, acetate, oxalate, and tartrate, sodium chloride, calcium, magnesium, and aluminium chlorides have been determined and the maximum potential of each osmotic system has been measured at 25°. The sign of the membrane charge has been determined by cataphoresis experiments, using finely ground suspended membrane material. The data show that the initial rate of osmosis bears a definite relationship to the electrical properties of the membrane system for practically all the salts examined. The anomalous effects obtained with collodion are very similar to those obtained with membranes of porcelain, gold beater's skin, calf's bladder, and parchment paper. The maximal and minimal values obtained with these different membranes do not come at exactly the same concentrations, but when the results are considered in the light of the exact condition of the electrical orientations of the different membrane systems, they are found to be closely comparable. It is also shown that the anomalous effects are somewhat related to a time factor. For example, the data for the osmosis of potassium carbonate at the end of a two-hour period, when plotted against the logarithm of the concentration, did not give an N-shaped curve, whilst the N-shape is pronounced in the curve obtained at the end of a twelve-hour osmosis period. This makes it appear probable that the process of diffusion is in some way responsible for the repressing effects noted at the intermediate concentrations. J. F. S.

Four Laws of the Mutual Influence of Salts on the Solubility. P. P. von Weimarn (*Kolloid Z.*, 1923, 32, 145—149).—The author discusses four laws of mutual influence of salts on solubility and shows the importance of these to the behaviour of colloidal solutions. The four laws are: (1) Nernst's law. The solubility of a salt is decreased by the presence of a second salt which has a common ion with the first. (2) Noyes's law. The solubility of a salt increases in the presence of a second salt which has no ion in common with the first salt. (3) The solubility of a salt in the presence of a second salt with a common ion commences to increase from a definite concentration of the second salt. The definite concentration is determined by the nature of the two salts and the solvent, and is lower the smaller the power of the solvent to break up the complexes formed. (4) When two or more salts are dissolved in a given solvent, a competition for the solvent between the salts takes place, so that a decrease in the solubility of the salt which takes up least of the solvent follows. The existence of the third law demands a new statement of Nernst's law, which is therefore now written: The solubility of a salt in the presence of a second salt with a common ion decreases when the concentration of the second salt does not exceed a definite value. J. F. S.

Relation between Molecular and Crystal Symmetry as shown by X-Ray Crystal Analysis. G. SHEARER (*Proc. Physical Soc.*, 1923, **35**, 81—100).—A theoretical paper, in which the methods of X-ray analysis, the nature of the elementary crystal lattice, and the meaning of axes and planes of symmetry in the lattice are discussed. It is shown that the methods of X-ray analysis enable the number of molecules associated with the unit cell to be determined. With the aid of this information an attempt is made to connect the symmetry properties of the crystal with this number and with the symmetry properties of the molecules from which the crystal is formed. The symmetry number for each of the thirty-two crystal classes is given, and is shown to mean the minimum number of asymmetric molecules necessary in the unit cell to satisfy the symmetry conditions. The relative orientations and positions of these molecules in the cell are discussed. It is suggested that this symmetry number is the actual number of molecules in the cell when the molecule is asymmetric; further that, if the molecule possesses symmetry, this symmetry appears also in the crystal, and the number of molecules in the unit cell is obtained by dividing the symmetry number of the crystal by the symmetry number of the molecule. Evidence is produced in support of these hypotheses, and examples are given of their application to inorganic and organic crystals. J. F. S.

Structure of Metal Crystals. Modification of the Powder Method of Determining the Structure of Metal Crystals. E. A. OWEN and G. D. PRESTON (*Proc. Physical Soc.*, 1923, **35**, 101—108).—Plates of aluminium, iron, copper, lead, and magnesium have been examined by means of a Bragg X-ray spectrometer, employing radiation from a molybdenum anti-cathode. The maxima observed in the spectra are sufficiently intense to measure with accuracy, and the crystalline structure of the materials examined is readily determined. The following data have been obtained: aluminium has a face-centred cubic lattice, the length of the side of the unit cube of which is $a = 4{\cdot}041$ Å. and the number of atoms associated with each elementary cube is $n = 3{\cdot}98$; iron has a centred cubic lattice, $n = 2{\cdot}015$ and $a = 2{\cdot}869$ Å.; copper has a face-centred cubic lattice, $a = 3{\cdot}628$ Å. and $n = 4{\cdot}06$; lead also has a face-centred cubic lattice, $a = 4{\cdot}983$ Å. and $n = 4{\cdot}11$, and magnesium has a hexagonal lattice, the side of the hexagon having a mean value $a = 3{\cdot}17$ Å. and $n = 0{\cdot}98$. J. F. S.

The Mesomorphic State of Matter. G. FRIEDEL (*Ann. Physique*, 1922, [ix], **18**, 273—474).—A new classification of liquid crystals according to their structure. Matter is capable of existing in two forms, neither crystalline nor liquid, for which the new designation, the *mesomorphic state*, is proposed. The first form is called the smectic phase, after the soaps which occur in this class, and the second, the nematic phase, on account of the linear discontinuities which are its principal feature. A short historical account of liquid crystals, and a summary of the substances giving rise to either or both of the two types are given.

The smectic and nematic phases, when they occur together, are always separated by a discontinuity, and the former is the phase which is stable at the lower temperature. The smectic form is always optically positive, but the latter may be divided into two classes, nematic proper and cholesteric, according to the sign of the rotation. The smectic phase possesses high viscosity and is rigid except in the direction of the optical axis, and displacement is accompanied by a change of structure. On the other hand, the nematic type is fluid, often more fluid than the liquid, and accommodates itself to movements within the film, brownian or otherwise. When the smectic phase is not homogeneous, as when the temperature is raised, there appears a new structure showing groups of lines which are always in the form of focal conics. The conics form groups of two, an ellipse and a hyperbola, and the focal groups are often systematically arranged inside a polygonal structure. This structure is discussed in detail. On cooling from the liquid or nematic state, the smectic phase makes its appearance in short rods, ornamented by focal groups; the nematic type gives droplets in similar circumstances. A magnetic or electric field is without action on the smectic phase, whereas the structural lines in the nematic phase are oriented so that the optical axis becomes parallel, and normal, respectively, to the lines of force. Another point of difference between the two forms is the behaviour on transition from the crystalline to the mesomorphic state. In both types, the new structure is based on the old, but whereas the old surfaces of separation of the crystals show focal conics in the smectic phase, the division in the nematic type is always absolute. The two kinds of complex structure possessed by the latter type are based on threads with no characteristic geometric form, and on centres which give rise to a spherolytic structure. The cholesteric type, which is optically negative, is only a special form of the optically positive variety, for there is a gradual change from the optically negative class to the normal nematic type. W. E. G.

The Cholesteric Type of Compounds. GEORGES FRIEDEL (*Compt. rend.*, 1923, **176**, 475—478).—The addition of very small amounts of a cholesteric substance to a substance, such as azoxyanisole or azoxyphenetole, having a nematic phase, impresses on the latter the characteristic properties of the cholesteric type. If it is admitted that the rotatory power of the cholesteric phase is due to a very high torsion round the normal to the positive optical axis, then the rotatory power, measured in the normal region of the spectrum, should be greater the smaller the torsion. This is shown to be the case for mixtures of azoxyanisole and cholesteryl acetate.

From a consideration of the behaviour of mixtures of azoxyanisole or azoxyphenetole or of methylbenzylidenebenzidine with colophony, it is shown that the addition, to a nematic substance, of any substance having molecular rotatory power gives rise to a cholesteric substance in which the two typical structures of this form of matter are seen. If the amount of the asymmetric sub-

stance exceeds a certain, generally very small, amount the structure with planes shows a very strong rotatory power of the type of ordinary cholesterol compounds, but if the amount of the asymmetric substance tends towards zero, there is a gradual passage from the cholesteric to the nematic characteristics. W. G.

Dielectric Constants of Colloidal Solutions. II. J. ERRERA (*Kolloid Z.*, 1923, **32**, 157—163).—A continuation of work previously published (A., 1922, ii, 694). The dielectric constant of a number of vanadium pentoxide sols has been determined under a variety of conditions. It is shown that the constant is increased by passing an alternating current through the solution, due to electric coagulation. Dilution of a sol causes an immediate decrease in the value of the dielectric constant, but, on keeping, the value increases with time; this is due to the partial solution of the disperse phase. Increasing temperature decreases the dielectric constant to an amount corresponding with the increase in the molecular motion and the degree of dispersion. The dielectric constant increases with increasing current strength and increasing wave-length in accordance with the increased directing force. Measurements of the electrical conductivity of the solutions show that the changes observed in the dielectric constant are real and not due to changes in the conductivity factor. The importance of the above results for the theory of electrical double refraction and anomalous dispersion is pointed out. J. F. S.

The Study of Soap Solutions. J. W. McBAIN (*Rep. Brit. Assoc.*, 1922, 360—361).—A review of the evidence for the existence of the ionic micelle and the theories arising therefrom. E. H. R.

Lyotropic Action in Processes of Solution of Colloids. N. P. PESKOV (*Kolloid Z.*, 1923, **32**, 163—166).—The action of the kations, ammonium, lithium, sodium, potassium, rubidium, and cæsium on the rate solution of arsenic sulphide, gold, and cupric sulphide sols in alkaline media has been investigated. It is shown in all cases that the lyotropic action of these kations is in the order $NH_4^{\cdot}|H_2O|Li^{\cdot}, Na^{\cdot}, K^{\cdot}, Rb^{\cdot}, Cs^{\cdot}$. The ammonium ion decreases the rate of solution very strongly, whilst the other ions increase it more the greater the atomic weight of the element. The effect of adding the chlorides of the alkali metals on the time required for the production of the blue colour in mixtures of sodium sulphite, sulphuric acid, and iodic acid has also been investigated, and found to have in all cases an accelerating action, the order of increasing acceleration being $Li^{\cdot}, Na^{\cdot}, K^{\cdot}, NH_4^{\cdot}, Rb^{\cdot}, Cs^{\cdot}$. With the exception of ammonium, the order is the same as that noted above. Similar experiments with coagulated arsenic sulphide and gold gave exactly the same order as was obtained with the uncoagulated sols, showing that the lyotropic action extends to macro-heterogeneous systems. A still coarser system, gold obtained by the reduction of gold chloride with hydrogen peroxide, furnished identical results, and finally gold powder dissolved more rapidly in the presence of rubidium chloride than in pure water. Hence it is shown that the

lyotropic action refers only to the solvent, and is manifested with all degrees of dispersion of the system. Adsorption only plays a part in so far as it may displace the action. J. F. S.

The Effect of Dissolved Substances on the Deposition of Colloidal Particles from a Solution by means of an Electric Current. RICHARD D. KLEEMAN (*Physical Rev.*, 1922, 20, 272—279).—The addition of 0·1—0·3% of sodium hydroxide, silicate, sulphate, phosphate, hydrogen phosphate or tartrate, potassium hydroxide, or tartaric acid to porcelain slip (a colloidal solution of clay, flint, and felspar in water) results in the formation of a solid instead of a semi-liquid deposit when it is subjected to an electric current. The increase in compactness of the deposit, obtained on the addition to the slip of one of the substances mentioned, was found to be intimately connected with the increase in fluidity of the slip produced by them. In explanation, it is assumed that the addition of a small amount of a substance to the slip decreases the radii of the spheres of action of the particles, or the spheres associated with the particles which do not penetrate into each other during their motion of translation. The fact that continued addition of the substance first precipitates some of the particles, mainly the flint and felspar, and then causes redissolution is explained in the same way. The equations of distribution of colloidal particles under the action of gravity are obtained. The experimental results indicate that the volume of the spheres of action of a particle in porcelain slip is about twice the actual volume of the particle. A. A. E.

Ultramicroscopic Method for the Measurement of the Velocity of Kataphoresis. H. R. KRUYT and A. E. VAN ARKEL (*Kolloid Z.*, 1923, 32, 91—95).—An apparatus is described whereby the velocity of kataphoresis of ultramicroscopic particles may be measured. From the measurements it is shown that the potential at the interface colloid–dispersion medium may be calculated. Using this apparatus, the velocity of kataphoresis of selenium sols has been determined at distances 0—900 mm. from the walls of the containing vessel. The potential at the interface is found to be 43 m.-volts. J. F. S.

Heterogeneous Equilibria between the Chlorides of Calcium, Magnesium, Potassium, and their Aqueous Solutions. I. WILLIAM BELL LEE and ALFRED CHARLES EGERTON (T., 1923, 123, 706—716).

Equilibria between the Acido- and Aquo-iridiumpentammines. ARTHUR B. LAMB and LAWRENCE T. FAIRHALL (*J. Amer. Chem. Soc.*, 1923, 45, 378—395).—Slight modifications have been made in Palmaer's method of preparing iridiumpentammine salts; these modifications give purer products and are more convenient (A., 1896, ii, 179). Chloropentammineiridium chloride has been shown to undergo no appreciable decomposition in aqueous solution at 100°. The velocity of transformation of chloro-, bromo-, iodo-, and nitrato-pentammines into the corresponding aquammines and *vice versa* has been measured at 95°, and in the case of the

bromo-ammines at 80°. All these transformations have been found to follow the course of a unimolecular reaction, and their velocity constants have been found to have the same relative magnitudes as the corresponding constants of the cobaltammines. The equilibria reached in these transformations have been investigated analytically. For this purpose, the method of McLean and Van Slyke (A., 1915, ii, 479) has been carefully studied and still further refined. The values for the equilibrium concentrations, thus found, are shown to be substantially in agreement with those calculated from the velocity measurements, and similar to those of corresponding equilibria among cobaltammines. They are all, however, markedly displaced from the aquo-side of the reaction, as compared with the corresponding cobaltammines. The values for the concentrations found in the bromo-bromide equilibrium have been shown to agree reasonably well with the requirements of an empirical equation similar to that found for the cobaltammines. This equation has the form $[C_B - C_{Cl'}]^{0.46}/C_P = K_2$ where C_B and C_P represent the total concentration of aquo- and acido-salts, respectively. The conclusion has therefore been drawn that, whilst the exchange of the central cobalt atom for an iridium atom in the ammines considered has produced a general displacement in the velocity and equilibria constants, it has produced no relative displacements. J. F. S.

Dynamics of the Formation of Nitriles from Acid Anhydrides and Amides. IV. Investigation of the Reaction between Acetamide and Benzoic Anhydride by Phase Rule Methods. Robert Kremann, Alois Auer, Viktor Oswald, and Alfred Zoff (*Monatsh.*, 1923, 43, 345—358).—The interaction of equimolecular quantities of acetamide and benzoic anhydride proceeds according to the simple equation : $CH_3{\cdot}CO{\cdot}NH_2 + (C_6H_5{\cdot}CO)_2O \rightleftharpoons CH_3{\cdot}CN + 2C_6H_5{\cdot}CO_2H$, no side-reaction (to produce acetylbenzoylimide) occurring (cf. A., 1922, ii, 748). The reaction was followed by the method previously employed by the author. The formation of an equimolecular compound (cf. this vol., i, 336) between acetamide and benzoic anhydride, melting at a temperature (84°) at which these two substances interact rapidly, caused difficulty in obtaining accurately the first few points on the temperature-freezing point curve. Other difficulties arose from the volatility of acetonitrile. The reaction studied is reversible, equilibrium (at 98°) being reached at 69% conversion from left to right of the above equation. The formation of the compound between acetamide and benzoic anhydride is thought to explain the fact that, from the results of the present investigation, benzoic anhydride appears to be a less effective dehydrating agent than acetic anhydride, whereas other results point to the contrary conclusion (cf. following abstract). E. E. T.

Dynamics of the Formation of Nitriles from Acid Amides and Anhydrides. V. The Study of the Reaction : 1 Benzoic Anhydride + 2 Acetic Acid $\rightleftharpoons$ 2 Benzoic Acid + 1 Acetic Anhydride. Robert Kremann and Wilhelm Rösler (*Monatsh.*, 1923, 43, 359—365).—The reaction studied proceeds from left to

right (at 77·5°) to the extent of about 65%, giving a reaction constant $K=6·4$. The reaction was studied by the usual method (freezing-point determinations at intervals, with subsequent reference to a freezing-point curve obtained from known mixtures, etc.), and it is shown that although, undoubtedly, two side reactions, producing the mixed anhydride, occur, these do not affect, to any extent, the figures given above for the main reaction.

E. E. T.

The Conditions of Reaction of Hydrogen with Sulphur. I. Direct Union. RONALD GEORGE WREYFORD NORRISH and ERIC KEIGHTLEY RIDEAL (T., 1923, **123**, 696—705).

The Propagation of Flame in Complex Gaseous Mixtures. V. The Interpretation of the Law of Speeds. WILLIAM PAYMAN (T., 1923, **123**, 412—420).

The Rate of Detonation in Complex Gaseous Mixtures. WILLIAM PAYMAN and NOEL STANLEY WALLS (T., 1923, **123**, 420—426).

The Effect of Pressure on the Limits of Inflammability of Mixtures of the Paraffin Hydrocarbons with Air. WILLIAM PAYMAN and RICHARD VERNON WHEELER (T., 1923, **123**, 426—434).

A Simple Form of Apparatus for Observing the Rate of Reaction between Gases and Liquids, and its Use for Determining the Rate of Solution of Oxygen by Water under Different Conditions of Mixing. H. G. BECKER (*Phil. Mag.*, 1923, [vi], **45**, 581—592).—The principle on which the apparatus is based depends on the changes in pressure which occur when a liquid is placed in contact with a closed volume of gas. The measurements of the absorption of oxygen were made with a suspension of ferrous hydroxide in water. Five different rates of stirring of the water were employed, ranging from zero to 1000 revolutions per minute. The process of adsorption followed a linear law showing that the deoxygenation of the water was complete in a few seconds. The rate of solution per unit area increases rapidly with increase in the rate of stirring, and tends to a maximum as the higher rates are reached. Gentle stirring of the under layers of the water increases the rate of solution as much as twenty-fold compared with stationary water. When in the quiescent state, the rate of solution of a gas by a liquid is liable to sudden unaccountable changes. The maximum rate of solution attained in these experiments was 0·0016 c.c. per min., which was about half that obtained by another method, previously reported (cf. A., 1919, ii, 510).

W. E. G.

The Velocity of the Absorption of Carbon Dioxide by Ammoniacal Solutions. PAUL RIOU (*Compt. rend.*, 1923, **176**, 581—583).—The influence of varying amounts of sodium and ammonium chlorides and sodium hydrogen carbonate on the

absorption of carbon dioxide by ammonium carbonate solutions was studied, and the results obtained are expressed by curves showing the c.c. of gas absorbed per second per sq. cm. of surface by ammonium carbonate solutions containing 0·04 g. mol. per 100 c.c. in presence of varying concentrations of the other salts. Sodium and ammonium hydrogen carbonates have the greatest retarding influence on the absorption, and ammonium chloride the least at 20°. The influence of temperature on the absorption in presence of ammonium and sodium chloride at different concentrations is also shown. With decreasing concentrations the maximum absorption velocity is displaced slightly on the temperature axis, being at about 20° with 0·5 g. mol. NH_4Cl per 100 c.c. and 35° with 0·1 g. mol. per 100 c.c. The maximum with sodium chloride solutions lies at about 50°. G. F. M.

The Antagonistic Action of Ions. H. Wastl (*Biochem. Z.*, 1922, **134**, 131—138).—The influence of the anions of various potassium salts on the time which elapses before the blue colour of starch iodide appears in the reaction between iodic acid and sulphurous acid (Landolt's reaction) has been studied. The results confirm Berczeller's observations that the reaction is accelerated by the anions in the order $I > Br > Cl > NO_3 > SO_4$. Sulphate is antagonistic to chloride, bromide, or iodide, the latter accelerating the reaction, the former retarding it. H. K.

The Velocity with which Carbon Monoxide Displaces Oxygen from Combination with Hæmoglobin. I. H. Hartridge and F. J. W. Roughton (*Proc. Roy. Soc.*, 1923, [*B*], **94**, ([*B*], 662), 336—367).—The reaction $CO + O_2\overline{Hb} \rightleftharpoons O_2 + CO\overline{Hb}$ is a reversible one, and the equilibrium constant has a value in light different from that in darkness. On this circumstance are based two methods for measuring the velocity constant of the reaction, a determination difficult to carry out directly as equilibrium is attained very quickly. In the first method, hæmoglobin solution containing oxygen and carbon monoxide flows through two glass tubes in series, one illuminated and the other in darkness. Measurements are made of the percentage of oxyhæmoglobin and carboxyhæmoglobin at various points in the illuminated tube by means of the reversion spectroscope (Hartridge, this vol., ii, 105). If the rate of flow is known, the time taken to reach the various points at which measurements have been made can be calculated, and hence the velocity constant of the reaction found. The second method consists in interrupting the illumination of the hæmoglobin contained in a trough, and measuring accurately the time taken for the change towards the new equilibrium to proceed a certain distance, as indicated by analysis by the reversion spectroscope. The values of k, the equilibrium constant, obtained by the two methods at 16° are 0·55 and 0·42, respectively, the difference being within the experimental error. The mean temperature coefficient as obtained by the two methods is 2·5, and log k is approximately inversely proportional to the temperature. W. O. K.

The Decomposition of Formic Acid by Sulphuric Acid. ERNEST R. SCHIERZ (*J. Amer. Chem. Soc.*, 1923, **45**, 447—455).—A study of the velocity of decomposition of formic acid by sulphuric acid, of different concentrations, at temperature intervals of 10° from 15° to 45°. The reaction is unimolecular and probably one of dehydration. The addition of small amounts of water to the reaction mixture markedly decreases the velocity of the reaction which, however, increases rapidly with rise in temperature. There is a marked irregularity in the temperature coefficients of the reaction for 91·8% sulphuric acid. The presence of copper, silver, potassium, sodium, or mercurous sulphates causes only a slight retardation of the reaction. Acetone and acetic acid act as inert diluents but hydrochloric acid increases the velocity of the reaction considerably. W. G.

Hydrolysis of Methyl *o*-Nitrobenzoate in Acid Solution. GERALD E. K. BRANCH and DONALD S. MCKITTRICK (*J. Amer. Chem. Soc.*, 1923, 45, 321—327).—The rate of hydrolysis of methyl benzoate and methyl *o*-nitrobenzoate, the rate of esterification of *o*-nitrobenzoic acid, and the position of the equilibrium in each case has been determined under the same conditions. The reaction mixtures contained 60% of methyl alcohol, 40% of water, 0·25*N*-sulphuric acid, and 0·1104 g.-mols. per litre of organic acid or ester. It is found that the equilibrium for the unsubstituted and the substituted compound lies at practically the same point. The esterification is found to be of a higher order than the corresponding hydrolysis. The rate of hydrolysis of methyl benzoate is found to be twenty times as great as that of methyl *o*-nitrobenzoate. This result is at variance with the results obtained by Kellas (A., 1898, i, 96) for alkaline solutions. The discrepancy is explained by assuming the reactions to be preceded by complex formation between the ester and the hydrogen- or hydroxyl-ion. As is to be expected, the nitro-group favours the formation of the complex with the hydroxyl-ion and the dissociation of that with the hydrogen-ion, and consequently accelerates the reactions in alkaline solution but retards those in acid solution. J. F. S.

Enzymatic Hydrolysis of Alkyl Glucosides. Determination of some Molecular Weights. H. COLIN and (MLLE) A. CHAUDUN (*Compt. rend.*, 1923, **176**, 440—442).—When to a given weight of a glucoside increasing amounts of a preparation of emulsin are added the weight of dextrose liberated in twenty-four hours gradually increases to a maximum beyond which any further addition of the enzyme does not cause any increase in the amount of dextrose liberated. In the cases of methyl, propyl, *iso*propyl, butyl, and *iso*butyl glucosides it is shown that the volume of the given enzyme preparation required to give the maximum hydrolysis in twenty-four hours is, within the limits of error of the experiment, inversely proportional to the molecular weight of the glucoside. W. G.

Dependence of the Velocity of Coagulation of Suspensoids on the Temperature. W. W. Lepeschkin (*Kolloid Z.*, 1923, 32, 166—167).—The temperature coefficient of the rate of coagulation of denatured albumin, arsenic trisulphide, and lecithin in the presence of alkali salts has been determined. The value of the coefficient in the case of arsenic sulphide is the smallest and is the same as that of the salt diffusion. Lecithin has a somewhat greater coefficient whilst that of albumin is greatest and has a value approximating to that of a chemical reaction. J. F. S.

Mechanism of the Catalysis of Hydrogenation by Nickel. Maitland C. Boswell (*Trans. Roy. Soc. Canada*, 1922, 16, III, 1—25).—By a quantitative study of the reduction of nickel oxide by hydrogen, and of the catalysis of the hydrogenation of ethylene by partially reduced nickel oxide, it is shown that oxygen necessarily present in a normal nickel catalyst exists partly in the form of nickel oxide in the interior of the catalyst particles and partly as negatively charged hydroxyl groups together with positively charged hydrogen on the surface nickel of the particles. Hydrogen absorbed during the reduction of nickel oxide, exists on the nickel surfaces with both positive and negative charges. The structure of the catalyst is represented by $(\mathrm{NiO})_x,\mathrm{Ni}(\overset{+}{\mathrm{H}}\overset{-}{\mathrm{OH}}\overset{+}{\mathrm{H}}\overset{-}{\mathrm{OH}}\ldots.)$ and the catalysis of the hydrogenation of ethylene by the following: (1) $(\mathrm{NiO})_x,\mathrm{Ni}(\overset{+}{\mathrm{H}}\overset{-}{\mathrm{OH}}\overset{+}{\mathrm{H}}\overset{-}{\mathrm{OH}}\ldots.)+\mathrm{C_2H_4}(\overset{+}{\mathrm{H}}\overset{-}{\mathrm{H}}) \longrightarrow (\mathrm{NiO})_x,\mathrm{Ni}(\overset{+}{\mathrm{H}}\overset{-}{\mathrm{OH}}) + \mathrm{C_2H_6} + \mathrm{H_2O}$. (2) $(\mathrm{NiO})_x,\mathrm{Ni}(\overset{+}{\mathrm{H}}\overset{-}{\mathrm{OH}}\overset{+}{\mathrm{H}}\overset{-}{\mathrm{OH}}) + (\overset{+}{\mathrm{H}}\overset{-}{\mathrm{H}}) \longrightarrow (\mathrm{NiO})_x,\mathrm{Ni}(\overset{+}{\mathrm{H}}\overset{-}{\mathrm{OH}}\overset{+}{\mathrm{H}}\overset{-}{\mathrm{H}}) + \mathrm{H_2O}$. (3) $(\mathrm{NiO})_x,\mathrm{Ni}(\overset{+}{\mathrm{H}}\overset{-}{\mathrm{OH}}\overset{+}{\mathrm{H}}\overset{-}{\mathrm{H}}) \longrightarrow (\mathrm{NiO})_{x-1},\mathrm{Ni}(\overset{+}{\mathrm{H}}\overset{-}{\mathrm{OH}}) + \mathrm{H_2O}$. A fourth reaction representing the mechanism of hydrogen absorption also occurs, and involves the addition of positive and negative hydrogen-ions derived from neutral hydrogen molecules to the complex on the right-hand side of reaction (1) to form the complex on the left-hand side of reaction (3). Of these reactions, (1) is very fast and (2) and (3) are very slow. The latter pair also represents the reactions occurring on continued reduction of nickel oxide by hydrogen. Finally, by such reduction all hydroxyl groups on the surface are removed and only absorbed hydrogen with positive and negative charges remains.

J. S. G. T.

The Catalytic Decomposition of Formic Acid in Acetic Anhydride. Ernest R. Schierz (*J. Amer. Chem. Soc.*, 1923, 45, 455—468).—Sulphuric, nitric, hydrochloric, hydrofluoric, phosphoric, and oxalic acids act as catalysts in the decomposition of formic acid in acetic anhydride, but owing to side reactions it is not possible to obtain quantitative data. Tertiary bases cause a similar catalytic decomposition and the velocity of decomposition corresponds roughly with the basicity of the base. A weak base like caffeine does not cause decomposition. Velocity constants have been determined for a number of bases at 50°. The reaction

is one of the first order and the velocity increases with the concentration of the catalyst. The decomposition by pyridine proceeds with different velocities in different solvents such as benzene, toluene, acetone, carbon tetrachloride, nitrobenzene, ethyl, amyl and *iso*butyl alcohols, amyl acetate, and benzaldehyde. Acetic acid has an inhibitory effect on the catalysis by brucine, strychnine, and morphine, but not on the catalysis by pyridine. This inhibitory effect may be used as a quantitative method for estimating acetic acid in its anhydride. In two cases, the joint effect of two bases was the sum of their separate effects. The author suggests a possible mechanism for the reaction by the formation of an intermediate compound. W. G.

The Constitution of the Atom. A. REYCHLER (*Bull. Soc. chim. Belg.*, 1922, **31**, 411—417; cf. A., 1922, ii, 279).—The author's previous formula for the calculation of atomic weights from atomic numbers, $A=2N+\beta N^2$, is now derived from theoretical considerations, and it is shown that the atomic radii of the elements of the helium group deduced by extrapolation from Bragg's crystal measurements are proportional to the cube roots of their atomic numbers. From a consideration of the energy changes involved when an electron is transferred from one shell to another, the author is able to derive Moseley's frequency formula, $\nu=\text{const.}(1/m^2-1/n^2)(N-b)^2$. H. H.

The Structure of the Atomic Nucleus. W. VAN DER BERG (*Chem. Weekblad*, 1923, **20**, 54—58).—A critical discussion of the results of Harkins (A., 1922, ii, 172). The packing effect of four protons in the helium nucleus corresponds with a loss of mass of 0·032 on the mass 4·032, or about 0·8%; a loss of mass is to be expected from the theory of relativity. The deductions of Lunn are criticised as being based on the assumption that Coulomb's law is valid within the nucleus, and as ignoring differences in mass due to the velocity of the nucleus.

The velocity required in an α-particle to disintegrate a helium nucleus is calculated as more than one-eighth the velocity of light; the fastest α-particle, that projected by radium C, has a velocity one-fifteenth that of light. The β-particle has a velocity approaching that of light, but its mass is insufficient; neither has any known electro-magnetic radiation a frequency high enough to effect the disintegration. Since there is no measurable loss of weight in the formation of carbon, oxygen, and heavier atoms from δ-particles, it should be possible to disintegrate these by bombardment.

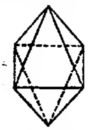
From a consideration of the atoms of low atomic weight, up to calcium, it appears that where elements of uneven atomic number contain, in addition to α-particles, both external and internal (binding) electrons, the stable configuration is $n\alpha$-particles with three protons and two external electrons. No stable configuration can be formed from two helium nuclei. It is clear that for the lighter elements, those having an even atomic number are much more stable than those having an odd atomic number, whilst the heavier elements are much less stable than the lighter. S. I. L.

The Number of Radiating Atoms of Various Dimensions within Gaseous Hydrogen, from the Point of View of Bohr's Atom Model. P. LASAREV (*Phil. Mag.*, 1923, [vi], **45**, 430—432).—On the Rutherford-Bohr theory, the radius of an electronic orbit moving round a hydrogen atom is given by $a=h^2\tau/4\pi^2me^2$. On account of the mutual influence of the electric fields of the atoms, τ cannot exceed 15, and thus the dimensions of the orbits will range between $2a=1\cdot1\times10^{-8}$ cm. ($\tau=1$) to $247\cdot5\times10^{-8}$ cm. ($\tau=15$). In star spectra, however, the existence of atoms with an electronic orbit of the order 33 is indicated. Calculations are made from the energy of definite spectral lines of the relative number of atoms of hydrogen gas possessing electron orbits of the different orders. Most of the electrons causing the radiation spring over from the third orbit to the second, and the quantity springing over from the fourth orbit to the second equals only 25% of the first quantity. Those from the fifth to the second orbit are only 17% of the number from the third to the second. Thus the quantity of springing electrons decreases with the distance of the electrons from the centre. W. E. G.

Compressibility, Internal Pressure, and Atomic Magnitudes. THEODORE W. RICHARDS (*J. Amer. Chem. Soc.*, 1923, **45**, 422—437).—A theoretical paper in which the respective bulks of the elements in combination have been evaluated from considerations of the compressibilities of the individual elements and the contraction which occurs during combination. With the help of Bridgman's accurately determined pressure volume curves for potassium and sodium (*Proc. Nat. Acad. Sci.*, 1922, **8**, 361) and the author's own earlier results of the compressibilities of bromine and chlorine (A., 1922, ii, 42), extrapolated by careful study of the nature of the curves [for which surprisingly concordant equations of the type $(p+P)(v-B)=K$ are derived], the values of the internal pressures existing in these salts, as well as the relative volumes of the components and the atomic diameters in combination, were calculated. J. F. S.

The Influence of the Atomic Nucleus on Valency, Orientation, and the Induced Polarity of Atoms. HERBERT HENSTOCK (*Chem. News*, 1923, **126**, 129—135).—A theoretical paper in which the alternate polarity of a chain of atoms is ascribed to a rotation of the nuclei and the inner electrons of the atoms. The nucleus of an atom is assumed to be a dipolar sphere, with the inner electrons situated at or near the poles, and according to the direction of the dipole within the atom, the valency bond will be either positive or negative. A strong outside influence may rotate the nucleus of a key atom, thus determining its polarity and inducing an opposite arrangement in a neighbouring atom. This in turn will determine the orientation of the next atom and so give rise to alternate polarity. The relationship between electrovalence and covalence is discussed. W. E. G.

Method of Representing Co-ordinated Compounds. T. M. LOWRY (*Chemistry and Industry*, 1923, **42**, 224—225).—The dis-

advantages of the conventional representation of the stereoisomerism of co-ordinated compounds, *e.g.*, potassium cobaltinitrite or cobalthexammine chloride, by a square pierced by an axis of fourfold symmetry, as suggested by Werner, or by the crystallographic projection of an octahedron, are briefly referred to. Alternatively the author suggests that such stereoisomerism should be graphically represented by the plane diagram of an octahedron obtained by drawing the customary hexagonal representation of the benzene ring, and joining the 2 : 4 : 6 positions by full straight lines, and, if desired, joining the 1 : 3 : 5 positions by dotted straight lines thus: . The usefulness of this method of representation is illustrated by diagrams showing the enantiomorphism of the different types of compounds to which Werner attributed asymmetry. More especially it is pointed out that enantiomorphs exhibiting optical activity, and in which three identical bivalent radicles are associated with a single atom of metal, can be readily depicted by using the two variants of Kekulé's formula for benzene.

J. S. G. T.

Change of Water of Hydration into Adsorbed Water during the Mechanical Subdivision of Crystal Hydrates. T. HAGIWARA (*Kolloid Z.*, 1923, 32, 154—156).—Weimarn has previously stated that the affinity of a substance for its water of crystallisation decreases as the size of the particles diminish. With the object of testing this statement, the author has determined the amount of water which the hydrate $Al_2O_3,3H_2O$ will retain at various temperatures in ordinary circumstances, and how this amount is affected by grinding the alumina with four times its weight of quartz. The experimental results show that Weimarn's hypothesis is in keeping with the facts, for example after heating a specimen of $Al_2O_3,3H_2O$ at 180° for five hours the material still retained 2·82 molecules of water, whilst heating the finely ground material at the same temperature for four hours removed all the water but 0·99 mol. per mol.

J. F. S.

Lecture Experiment Demonstrating Adsorption. H. G. TANNER (*J. Amer. Chem. Soc.*, 1923, 45, 437—438).—A quantity of a solution of malachite green oxalate is poured into a clean beaker and immediately poured away. The beaker is then washed with large volumes of water. Then a few c.c. of water are poured into it, shaken round the walls, and poured into a test-tube. The solution is quite colourless. A few c.c. of glacial acetic acid are next added to the beaker, shaken round the walls, and poured into a test-tube. The solution in this case is distinctly green, due to malachite-green which has been adsorbed on the walls of the beaker and dissolved in the acetic acid.

J. F. S.

Inorganic Chemistry.

Preparation of Active Hydrogen. Y. VENKATARMAIAH (*J. Amer. Chem. Soc.*, 1923, **45**, 261—264).—An active form of hydrogen, which will react with cold sulphus to produce hydrogen sulphide may be produced by the continuous burning of oxygen in hydrogen, by the surface combustion of hydrogen and oxygen on a platinum surface, and by a high tension arc in hydrogen between silver electrodes. When gold or platinum electrodes were used in place of silver electrodes in the last method, no active hydrogen, as tested by the non-formation of hydrogen sulphide, was obtained. The author considers that the failure in this case is due to the adsorption of the gas by the thin film of these metals which is deposited on the walls of the reaction vessel during the experiment. Success in all the experiments depends on the temperature being kept low. J. F. S.

Ethyl Alcohol as a Stabiliser for Hydrogen Peroxide. (MME) LISIEVICI-DRAGANESCU (*Bul. Soc. Chim. România*, 1922, **4**, 65—68).—Ethyl alcohol is a satisfactory stabiliser for hydrogen peroxide. Added in the proportion of 10% to hydrogen peroxide of 10 vols. strength, a diminution of only about 0·3% was observed after four months with a sample stored in open glass bottles and exposed to sunlight, and only 0·1% in closed coloured glass bottles. To effect the same stabilisation with "perhydrol," the addition of 30% of ethyl alcohol was necessary. G. F. M.

The Magneto-chemical Effect. IV. A. N. SCHTSCHUKAREV (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 109—122).—Chlorine, produced by the electrolysis of barium or cæsium chlorides in a magnetic field, disintegrates, giving rise to positive particles, having a mass of about 0·013 that of a hydrogen atom, and to negative particles which are shown to be ordinary electrons. This decomposition is explained as being due to the effect of the magnetic field on the chlorine produced under conditions of changed valency. R. T.

Reaction between Silver Perchlorate and Iodine: Chlorine Tetra-oxide. M. GOMBERG (*J. Amer. Chem. Soc.*, 1923, **45**, 398—421).—An investigation of the action of iodine and bromine on dry silver perchlorate in anhydrous solvents has been carried out with the object of ascertaining whether a substance of the formula $(ClO_4)_x$ could be prepared. The reaction $2AgClO_4+I_2=2AgI+2(ClO_4) \longrightarrow (ClO_4)_x$ is found to take place in ethereal solution, but in this case there is a very small amount of a labile iodine compound also formed, which is assumed to be iodine tetra-oxide, produced according to the equation $ClO_4+I \longrightarrow IO_4+Cl$. This iodine compound is very unstable and decomposes readily into iodine and oxygen, so that a solution of pure chlorine tetra-oxide in ether is readily obtained. It was found advisable in the preparation to use solutions not exceeding $0{\cdot}1N$. With solutions of this concentration, the properties of the new oxide have been

investigated. The substance is colourless, and is stable in ether solution. It does not volatilise in the ether vapour. It is probably bimolecular, $(ClO_4)_2$. The chemical activity of the substance would indicate that there is a considerable dissociation into single molecules, but this point has not been investigated. It is readily hydrolysed, yielding ultimately perchloric acid as the only product, but reasons are given for assuming that the primary course of the reaction with water is $2ClO_4+H_2O=HClO_4+HO{\cdot}ClO_4$. It liberates iodine from iodides, but not in equivalent amount. It reacts quantitatively with zinc and magnesium, forming perchlorates; with iron, tin, and copper, forming salts of the metal of lower and higher valency. It acts slowly and incompletely on cadmium, bismuth, and silver. Ethereal solutions of anhydrous perchloric acid and ethyl perchlorate have been submitted to the tests which are characteristic of chlorine tetra-oxide and found to respond to them in a manner entirely different from chlorine tetra-oxide.

J. F. S.

Atomic Weight of Selenium. P. Bruylants and J. Dondeyne (*Bull. Acad. roy. Belg.*, 1922, [v], 8, 387—405).—A previous determination was made in 1912 (A., 1913, ii, 500) and gave the figure 79·18. The weight of a normal litre of hydrogen selenide has been determined at pressures of 1, 0·6, and 0·3 atmosphere, the three values being, respectively, 3·6721, 3·65732, and 3·64407 g. The atomic weight of selenium is calculated, making use, in connexion with the compressibility values, of the two methods recommended by Guye (A., 1919, ii, 318), and taking the weight of a normal litre of oxygen as 1·4289 (Moles and Gonsalez, A., 1921, ii, 546). The difference between the new value of the atomic weight, 79·37, and that previously obtained is due to three causes: (*a*) The divergence of the compressibility between 0 and 1 atmosphere A_0' is, by Guye's method, 0·01083, whilst the value of A_0' calculated from direct measurements of pv at different pressures and using Berthelot's formula is 0·01302. Guye's method is preferable, owing to the high compressibility of hydrogen selenide. (*b*) The 1912 determinations of compressibility (from measurements of pv) give A_0' 0·01191, the density figures giving A_0' 0·01083. (*c*) In 1912, the local value of g was not known, this difficulty being surmounted by actually determining the weight of a normal litre of oxygen.

These three causes of difference all act in the same direction. The above figure (79·37) will therefore be subject to further correction when new data (for compressibility and weight of normal litre of hydrogen selenide) are available.

The paper contains a very complete table of vapour pressure measurements from t—78·01° (p 82·89 mm.) to t—20·77° (p 1799·0 mm.). From these results, the following constants are obtained: b. p.—41·2°/760 mm.; triple point at p 203·3 mm., t—65·9°; molecular latent heat of vaporisation at —41·2°, L 4·76. The boiling points of hydrogen selenide and carbon disulphide give a constant T_1/T_2 ratio between pressures of 230 and 1550 mm. E. E. T.

Catalysis in Homogeneous Gas Reactions: (I) The Catalysis of Formation of Nitrosyl Chloride by means of Bromine. A. Kiss (*Rec. trav. chim.*, 1923, **42**, 112—144).—The preparation of nitrosyl chloride by combination of nitric oxide and chlorine in presence of bromine takes place with preliminary formation of nitrosyl bromide. Measurements of the velocity of reaction between nitrosyl bromide and chlorine were carried out at temperatures ranging from 0° to 100° and show the reaction to be a clean, rapid gas reaction of the third order. It is accelerated by the presence of water vapour, although water does not act as a catalyst in the reaction between nitric oxide and chlorine at 18°. The formation of nitrosyl chloride either directly or through the intermediate stage of nitrosyl bromide is not affected by light; the direct formation is stimulated by the catalytic effect of a rough surface. The reaction velocity is not affected by the presence of hydrogen chloride or carbon dioxide and if light is excluded both hydrogen and carbon monoxide are without effect. In the case of the reaction between nitrosyl bromide and chlorine, no alteration is brought about by carbon dioxide. H. J. E.

A Low Temperature Electrolyte. Worth H. Rodebush and Theodore O. Yntema (*J. Amer. Chem. Soc.*, 1923, **45**, 332—337).—When nitric oxide and hydrogen chloride mixtures are submitted to the temperature of liquid air an intensely purple coloured solid is produced. This solid melts to a purple liquid, which between the temperatures 120° K. and 130° K. has a specific conductivity of more than 10^{-3} ohms, a value which is about the same as that of 0·01*N*-potassium chloride solution. Attempts to ascertain the composition of this substance were unsuccessful, but it is shown that the vapour pressure of nitric oxide from the purple solid is not appreciably less than that of pure liquid nitric oxide. This indicates that the complex is an exceptionally unstable one. The range over which it exists is small, being roughly between 120° K. and 130° K. It is suggested that the complex is of the form $[NOH]^+Cl^-$, and that it is one of the type of compounds containing an odd number of electrons and therefore, according to Lewis's hypothesis (A., 1916, ii, 310), is highly coloured. J. F. S.

Behaviour of Phosphoric Oxide towards Water. A Direct Method for the Preparation of Tetraphosphoric Acid. M. A. Rakusin and A. A. Arsenéev (*Chem. Ztg.*, 1923, **47**, 195).—After the violent reaction resulting from the addition of phosphoric oxide to water and formation of orthophosphoric acid has subsided, further quantities are gradually added until the amount reaches about 520% of the water present. After keeping for five days, crystals of tetraphosphoric acid, $H_6P_4O_{13}$, separate from the syrupy liquid. This acid has previously only been prepared in the form of its salts. It melts at 34°, and has d^{15} 1·8886. G. F. M.

The Solubility of Phosphoric Oxide in Ethyl and Methyl Alcohols. M. A. Rakusin and A. A. Arsenéev (*Chem. Ztg.*, 1923, **47**, 178). Phosphoric oxide dissolves readily to the extent

of 60% in ethyl and methyl alcohols with the development of heat. Considerably greater quantities of the oxide dissolve in the resulting liquids, on continued stirring and heating, up to 295 g. in the case of methyl alcohol giving a liquid of d^{15} 1·5437 and up to 258 g. in the case of ethyl alcohol giving a liquid of d^{15} 1·5894. These liquids react acid and do not boil on adding water, or give a precipitate with silver nitrate solution.

Phosphoric oxide causes phenol, menthol, and similar substances to dissolve in chloroform without apparently entering into any reaction with them. If the solutions are left for several days and the chloroform is then removed by a current of dry air, the phosphoric oxide and the phenol are recovered unchanged. A. R. P.

Studies in Hypophosphorous Acid. V. Its Reaction with Silver Nitrate. ALEC DUNCAN MITCHELL (T., 1923, **123**, 629—635).

Reducing Action of Arsenious Acid. MORITZ KOHN (*Monatsh.*, 1923, **43**, 367—371).—Silver nitrate is completely reduced to metallic silver in ammoniacal solution by arsenious acid, which is oxidised to arsenic acid. The reduction is not affected by the addition of neutral salts such as sodium nitrate or sulphate, but is hindered by ammonium sulphate, which causes a decrease in the concentration of hydroxyl-ions. The reduction of cupric sulphate by arsenious acid in presence of aqueous ammonia is not influenced by neutral salts such as potassium chloride or nitrate.
E. E. T.

Phosphorescent Boric Acid. ERICH TIEDE and ALFRED RAGOSS (*Ber.*, 1923, **56**, [*B*], 655—666; cf. Tiede, A., 1921, ii, 75; Tiede and Wulff, A., 1922, ii, 245).—It has been shown previously that intense phosphorescence is produced by the presence of certain organic substances in partly dehydrated boric acid. It is now found that similar products can be derived from boric acid and from completely dehydrated boron trioxide. Products derived from boric acid are obtained by crystallising the acid from water or acetone containing a small amount of the desired organic substance, *e.g.*, terephthalic acid, whereas those from boron trioxide are prepared by drying a mixture of hydrated boric acid and the required impurity over phosphoric oxide at 200°. Since boric acid readily becomes "infected" by the organic impurities present in the air, it is necessary to work under particular conditions which are described in detail in the original. Phosphorescence is excited by exposure to the light of a mercury lamp or iron–carbon arc; it does not generally persist during more than two minutes, the greatest diminution in intensity being observed during the first thirty seconds.

The activating effect of a large number of organic compounds has been examined. Aliphatic compounds do not exert an appreciable effect unless they have become decomposed to some extent. The presence of an aromatic nucleus or condensed system appears to be necessary. The colour of the emitted light depends almost

entirely on the nucleus which is present, with increasing complexity of which it is displaced towards the red. The presence of substituents greatly influences the intensity, but not the colour of the emitted light. Two substituents present simultaneously have their maximum action when in the para-position to one another, their minimum effect in the ortho-position. Saturated side chains, hydroxyl, and sulphonyl groups are feebly activating, the amino-group is inactive by reason of salt formation, and carboxyl greatly increases the brightness, particularly in the presence of a second carboxyl or of one of the feebly activating groups. Coloured substances seldom excite emission. Chlorinated compounds cause an extraordinary shortening of the period of phosphorescence. The presence of bromine, iodine, or the nitro-group inhibits phosphorescence.

Both physical and chemical examinations lead to the conclusion that the organic molecule is to be regarded as causative of the luminescence, and that the boric acid provides the necessary physical conditions. The presence of compounds derived from boric acid and the organic component is in many cases possible and probable, but these substances, *e.g.*, triphenyl borate and tri-β-naphthyl borate, are not in themselves phosphorescent.

The physical characteristics of boric acid phosphors have been described in detail by Tomaschek (A., 1922, ii, 763). It is, however, pointed out that the absorption spectra of organic substances in boric acid are similar to those in alcohol, and that phosphorescence of the boric acid phosphors is excited by rays of the same length as those absorbed; the emission spectra in boric acid and in alcohol are compared. H. W.

The Hydrates of Krypton and Argon. R. DE FORCRAND (*Compt. rend.*, 1923, **176**, 355—358).—The dissociation pressures of the hydrate of krypton as measured at various temperatures are 14·5 atmos. at 0°, 23·5 atmos. at 4·8°, 38·7 atmos. at 10·3°, and 47·5 atmos. at 12·5°. At 13°, the hydrate could not be obtained even with a pressure of 100 atmos. The critical temperature of decomposition of the hydrate is thus between 12·5° and 13°. From the above data the formula of the hydrate is calculated as being $Kr,5H_2O$.

A redetermination of Villard's value of the dissociation pressure of argon hydrate (A., 1897, ii, 31) gives the value as 98·5 atmos. at 0·2°, Villard's value thus being too high. From this and the value 210 atmos. at 8° the formula for this hydrate is calculated as being $Ar,5\frac{1}{2}H_2O$. W. G.

Perchlorates of the Alkali and Alkaline-earth Metals and Ammonium. Their Solubilities in Water and Other Solvents. H. H. WILLARD and G. FREDERICK SMITH (*J. Amer. Chem. Soc.*, 1923, **45**, 286—297).—The perchlorates of calcium, strontium, barium, magnesium, lithium, sodium, potassium, rubidium, cæsium, and ammonium have been prepared and investigated. The method of preparation in all cases but that of ammonium consists in evaporating the chloride or nitrate to dryness with an excess

of perchloric acid. The ammonium salt was prepared by leading ammonia into a dilute solution of perchloric acid. The solubility of the salts has been determined at 25° in water, methyl alcohol, ethyl alcohol, *n*-propyl alcohol, *n*-butyl alcohol, *iso*butyl alcohol, acetone, ethyl acetate, and ethyl ether. The density of the solvents and saturated solutions at 25°, and the solubility in each solvent, in grams per 100 c.c. and per 100 g. of solvent and solution and in g.-mols. per 100 c.c. and per 100 g. of solvent and solution are recorded in a number of tables. J. F. S.

Inorganic Luminescence Phenomena. V. Preparation and Properties of Phosphorescent Sulphides of Sodium and Rubidium. ERICH TIEDE and HERBERT REINICKE (*Ber.*, 1923, **56**, [*B*], 666—674).—In continuation of previous work (Tiede and Richter, A., 1922, ii, 215), the sodium and rubidium sulphide phosphors have been examined. As in the case of the phosphors of the sulphides of the alkaline-earth metals, the presence of a trace of a heavy metal appears necessary for the development of phosphorescence.

Attempts to prepare sodium sulphide by the direct union of sulphur vapour with sodium, by the use of carbon disulphide as in the case of magnesium sulphide (*loc. cit.*), from the azide or by the reduction of sodium sulphate with hydrogen, did not yield a sufficiently pure product. Success was, however, obtained by dissolving sodium hydroxide in absolute alcohol at the atmospheric temperature, dividing the filtered solution into two nearly equal portions, saturating the smaller portion with hydrogen sulphide, uniting it with the second portion, and crystallising sodium sulphide pentahydrate from the mixture as rapidly as possible. The product is dried in small portions over phosphoric oxide at 55°, and is subsequently heated at 600—650° in a graphite boat in a current of pure, dry nitrogen. The material prepared in this manner contains 95% of sodium sulphide, the remainder being composed of sodium hydroxide and a little sodium oxide, the presence of which is regarded as advantageous. When excited by the light of the mercury lamp it shows a faint, ill-defined phosphorescence, whereas specimens prepared from the technical sulphide are either non-phosphorescent or, more frequently, emit a relatively bright green light. The active agent in causing the sulphide to phosphoresce is iron which exerts its maximal action when present in traces much smaller than those generally necessary to produce similar effects; the introduction of suitable traces of the metal is effected by the addition of ferric chloride to the original sodium hydroxide solution. The induced phosphorescence is green, whereas that due to copper is pale yellow. The emission spectrum of sodium sulphide iron phosphor exhibits a narrow green band at 505—560 $\mu\mu$, whereas that of the corresponding copper phosphor has a broad band at 510—650 $\mu\mu$ with a maximum at about 550 $\mu\mu$.

It is remarkable that iron should be the excitant with sodium sulphide phosphors, since it has been found to be inactive with the sulphides of the second group at the concentrations examined

previously. New experiments on the action of much smaller amounts of iron on highly purified zinc sulphide indicate that the metal is active under these conditions.

Attempts to apply the method used in the preparation of sodium sulphide to that of the sulphides of lithium, potassium, or rubidium did not meet with success. Phosphorescent mixtures of rubidium sulphide and sulphate are prepared by the reduction of rubidium sulphate in a graphite boat by hydrogen at about 650°. The emitted light is bluish-red. The preparations decompose very readily. The amount of material available was insufficient to permit the certain identification of the exciting agent which appears to be effective at very small concentrations. H. W.

The Action of Alcohol on the Sulphates of Ammonium. HORACE BARRATT DUNNICLIFF (T., 1923, **123**, 476—484).

Reaction between Selenium and Silver Nitrate in Aqueous Solution. F. GARELLI and A. ANGELETTI (*Atti R. Accad. Lincei*, 1922, [v], **31**, ii, 440—445).—The authors are unable to confirm Guyot's statement (this Journal, 1871, 660) that, from neutral or acid solutions of salts of the metals, selenium dissolved in carbon disulphide precipitates only silver as silver selenide. In aqueous solutions the silver may be precipitated completely if excess of selenium is used and the liquid is boiled, the reaction corresponding with the equation: $4AgNO_3+3Se+3H_2O=2Ag_2Se+H_2SeO_3+4HNO_3$ (cf. Senderens, A., 1887, 331). From a neutral solution containing silver, lead, and mercurous or mercuric nitrate, the silver may be precipitated completely in this way, the amount of selenium added being at least twice that of the silver in solution, and the liquid being boiled for fifteen minutes and filtered when cold. The precipitate is heated with nitric acid and the silver estimated as chloride.

Before precipitating selenium from a nitric–hydrochloric acid solution of selenious acid, Treadwell recommends that the liquid be evaporated to dryness to expel excess of nitric acid. This procedure, however, involves loss of selenium owing to the volatility of selenious acid. The addition of alkali chlorides, as suggested by Fresenius, does not entirely overcome this difficulty. If, however, oxidation is effected by nitric acid alone, this may be eliminated by evaporation and the residue then taken up in hydrochloric acid without appreciable loss of selenium. T. H. P.

Hydration of Anhydrite. G. WEISSENBERGER (*Kolloid Z.*, 1923, **32**, 181—192).—The hydration of anhydrite has been investigated by following the hardening of the material in the presence of water. It is found that the rate of hydration is accelerated by the presence of ferrous sulphate and other catalysts. The rate of hydration also depends on the size of the particles. When the size of the particles is greater than a definite maximum value anhydrite is not hydrated, but when the particles are very small water is taken up readily. The following substances are shown to be definite compounds involved in the process of the

hydration of anhydrite: gypsum, $CaSO_4,2H_2O$; soluble anhydrite, $CaSO_4$; anhydrite, $(CaSO_4)_2$; and the hemihydrate, $2CaSO_4,H_2O$.
J. F. S.

Suspensions of Particles of Barium Sulphate of Various Sizes Examined by Transmitted and Reflected Light. AAGE W. OWE (*Kolloid Z.*, 1923, 32, 73—77).—Suspensions of barium sulphate in glycerol, mixtures of alcohol and glycerol and water and glycerol have been examined by both reflected and transmitted light. It is shown that the degree of turbidity as determined nephelometrically and also by transmitted light is dependent not only on the size of the particles but also on the composition of the dispersion medium. This dependence is due chiefly to changes of the index of refraction of the solvent and to the changes in the form of the combined particles. The degree of turbidity, obtained nephelometrically in pure glycerol, reaches a maximum value with particles somewhat less than 200 $\mu\mu$. In aqueous glycerol the maximum is probably displaced toward larger particles. The degree of turbidity, as obtained by means of transmitted light, increases steadily with increasing size of particles at least up to 1000 $\mu\mu$. The maximum which must of necessity exist lies probably in the region of particles having a size of several thousand $\mu\mu$.
J. F. S.

[**A Simple Method for the Preparation of Highly Phosphorescent Zinc Sulphide.**] ERICH TIEDE and ARTHUR SCHLEEDE (*Ber.*, 1923, 56, [*B*], 674—675).—In a recent communication (this vol., ii, 75), Schmidt has described the preparation of highly phosphorescent zinc sulphide, and has been drawn to the conclusion that its phosphorescence is inhibited by the presence of metals which yield black sulphides. This observation is directly opposed to the observations of Tomaschek (A., 1921, ii, 588). It is pointed out that Schmidt's procedure does not give any guarantee that the necessary amounts of copper are not introduced with the many salts employed and that it is therefore quite possible that subsequent additions of the element may cause its concentration to exceed the narrow limits required for optimal effect. A specific action in Schmidt's method cannot be attributed to the chlorides of the alkaline-earth metals and magnesium, since they can be replaced by the alkali chloride; the chloride is the important component. H. W.

The Action of Water and Steam under Pressure on some Soda-Lime-Silicate Glasses. F. W. HODKIN and W. E. S. TURNER (*J. Soc. Glass Tech.*, 1922, 6, 291—308).—Four soda-lime-silicate glasses having the approximate compositions

$$6SiO_2,0{\cdot}3CaO,1{\cdot}7Na_2O,$$

$6SiO_2,0{\cdot}7CaO,1{\cdot}3Na_2O$, $6SiO_2,0{\cdot}8CaO,1{\cdot}2Na_2O$, and $6SiO_2,CaO,Na_2O$ were subjected to the action of water and steam at pressures varying from 2 to 25 atmospheres above normal. The action of steam on these glasses is considerable, being greater than that of water at the higher pressures in the case of the glass having the

lowest lime content. Corrosion diminishes as the amount of lime is increased and the amount of sodium oxide decreased. The glass with the highest lime content was unattacked by steam or water in three hours at 2 to 4 atmospheres. The incrustation formed as a result of corrosion was harder the greater the lime content; a gelatinous layer was formed beneath the incrustation on the glass containing only 0·3CaO at 15 atm. pressure. Since the loss in weight recorded was less than the total alkali found in the water, it is clear that the glass absorbs a considerable quantity of water. The character of the corrosion, which clearly brings out pouring and moulding lines, is influenced markedly by the condition of the surface. The autoclave test is considered too severe for soda–lime–silicate glasses which are only required to resist the action of boiling water. E. H. R.

The Crystal Structure of the Alums. RALPH W. G. WYCKOFF (*Amer. J. Sci.*, 1923, 5, 209—217).—Studies of the Laue and spectrum photographs of potassium and ammonium aluminium alums were undertaken with a view to determine the space grouping of the alums. The hemihedral nature of the crystal structure is evident at once from the photographs, and from a study of the reflections from planes with one index zero, it is shown that the corresponding space group is T_h^6, rather than T_h^2. There are four molecules with the composition $R'R'''(SO_4)_2,12H_2O$ in the unit cell, and in this space group the four sulphate oxygen atoms cannot be exactly alike. Three of these atoms will be similarly placed, but the fourth will be different from the other three. The twelve water molecules fall in two groups of six each. The positions of the K or N and the Al and S atoms are given, but no attempt has been made to locate those atoms having variable parameters. The hydrogen atoms of the ammonium groups cannot be arranged in a chemically plausible radicle which will possess a symmetry in keeping with the rest of the crystal. The spectrographic observations show that unaided spectrometer measurements are insufficient for the determination of crystal structure. W. E. G.

Some Properties of Manganese Dioxide. A. DE HEMPTINNE (*Bull. Acad. roy. Belg.*, 1922, [v], 8, 71—75).—Manganese dioxide is slowly reduced by hydrogen at room temperatures, to give a product which slowly re-oxidises in the air. The dioxide rapidly absorbs hydrogen sulphide from a mixture of this gas with hydrogen, manganese sulphides being formed. The absorption is much more rapid than with dry hydrogen sulphide alone, although in presence of moisture this gas is readily absorbed by manganese dioxide. E. E. T.

Cementation by means of Boron. N. PARRAVANO and C. MAZZETTI (*Atti R. Accad. Lincei*, 1922, [v], 31, ii, 424—425).—When steel is heated at 900° in an atmosphere of boron chloride and hydrogen, it becomes coated with a layer of very hard alloy rich in boron and capable of cutting glass. Nickel also undergoes cementation under these conditions. T. H. P.

The Constitutional Diagram of the Iron–Carbon–Tungsten System. SIGEAKI OZAWA (*Sci. Rep. Tôhoku Imp. Univ.*, 1922, **11**, 333—350).—There is only one compound in the iron–tungsten system, viz. Fe_2W. In the iron–carbon–tungsten system this compound and iron carbide are mutually soluble at certain concentrations and the resulting solution splits up with the simultaneous separation of tungsten carbide, WC. A ternary eutectic containing 15% W, 3·6% C, and 81·4% Fe is formed and melts at 1065° (cf. *J.S.C.I.*, 1923, April). A. R. P.

Constitution of Ferric Oxide Hydrosol from Measurements of the Chlorine and Hydrogen Activities. FREDERICK L. BROWNE (*J. Amer. Chem. Soc.*, 1923, **45**, 297—311).—Using a calomel electrode as comparison electrode the chloride-ion activity has been measured in solutions of ferric chloride and in ferric oxide sols of various concentrations and widely varying purity. A method is described for using the hydrogen electrode in the presence of dilute solutions of ferric chloride, and this has been used for the measurement of the hydrogen-ion activity in ferric oxide sols. Ferric oxide sols having a total iron concentration of about 0·5 g. equiv. per litre and a purity of less than 14 (purity=g. equiv. Fe/g. equiv. Cl) contain ferric chloride and hydrochloric acid in the aqueous phase and the dispersed ferric oxide carries considerable amounts of adsorbed ferric chloride and hydrochloric acid. The adsorption of ferric ion and hydrogen-ion is greater than that of chloride-ion, thus giving the dispersed phase a positive charge. At higher purities, the adsorption of ferric-ion and hydrogen-ion is complete and the aqueous phase contains only chloride-ion, the "kations" for which are the dispersed particles. At lower concentration of total iron, ferric-ion and hydrogen-ion disappear from the aqueous phase at somewhat lower purity and at higher concentrations at high purity. The effect of dextrose on the freezing point of ferric oxide sol shows that practically all the water present in the sol acts as solvent for substances dissolved in the sol. Tables are given showing the concentrations of chloride-ion and its distribution between ferric chloride and hydrochloric acid in sols of widely varying purity and concentration, as well as the total chloride compounds adsorbed by the ferric oxide. J. F. S.

The Higher Oxide of Nickel. OWEN RHYS HOWELL (T., 1923, **123**, 669—676).

The System Chromium Trioxide–Nitric Acid–Water. STANLEY AUGUSTUS MUMFORD and LIONEL FELIX GILBERT (T., 1923, **123**, 471—475).

The Adsorption of Stannous Chloride by Stannic Acid. GEORGE ERNEST COLLINS and JOHN KERFOOT WOOD (T., 1923, **123**, 452—456).

Constitution of Black Maketu Sand. C. J. SMITHELLS and F. S. GOUCHER (*Nature*, 1923, **111**, 397; cf. Scott, T., 1923, **123**, 311).—Careful chemical and *X*-ray analysis of the black sand from

Maketu, N.Z., confirms Bohr's conclusion that no new element is present. A residue insoluble in sulphuric acid and fused sodium hydrogen sulphate was attacked by potassium hydrogen sulphate, and was found to contain iron and aluminium in equal parts (cf. Scott, T., 1923, **123**, 881). A. A. E.

Studies on Metal Hydrides. The Electrolytic Formation of Stibine in Sulphuric Acid and in Sodium Hydroxide Solution. HENRY JULIUS SALOMON SAND, EDWARD JOSEPH WEEKS, and STANLEY WILSON WORRELL (T., 1923, **123**, 456—470).

Perchlorates of Bismuth and Antimony. FR. FICHTER and ERNST JENNY (*Helv. Chim. Acta*, 1923, **6**, 225—231).—The method described by Muir (this Journal, 1876, i, 878) for the preparation of a perchlorate of bismuth, which is reproduced in the text-books, is attended with serious danger of explosion, especially when bismuth powder is dissolved in 70% perchloric acid. By dissolving bismuth powder very carefully in 40% perchloric acid a solution was obtained similar to that obtained by dissolving bismuth oxide in 70% acid. When this solution is evaporated in a vacuum desiccator, *bismuth perchlorate*,

$$Bi(ClO_4)_3,5H_2O,$$

is obtained in small, hexagonal tables which rapidly change in moist air into a bismuthyl salt. When an aqueous solution of the normal perchlorate is evaporated slowly, *bismuthyl perchlorate trihydrate*, $BiO{\cdot}ClO_4,3H_2O$, is obtained in aggregates of doubly refracting prismatic needles. It is very unstable and has a great tendency to change even in the mother-liquor into the *monohydrate*, $BiO{\cdot}ClO_4,H_2O$. This is the most stable salt and separates from all solutions not too concentrated with respect to perchloric acid. It forms very hygroscopic, rhombohedral crystals. The anhydrous salt, obtained by drying the monohydrate at 80—100°, is a white powder, differing from that described by Muir in being completely soluble in water. When concentrated perchloric acid is saturated with bismuth oxide, a mass of crystals separates, the composition of which approximates to $OH{\cdot}Bi(ClO_4)_2,H_2O$.

A perchlorate of antimony is obtained by dissolving antimony oxide in ten times its weight of 70% hot perchloric acid. Too high a temperature causes oxidation to antimonic acid. On cooling, antimonyl perchlorate separates in small needles having the composition $SbO{\cdot}ClO_4,2H_2O$. Some preparations were anhydrous. E. H. R.

Formation of Colloidal Gold Solutions by Means of Electrical Spark Discharges. W. NAUMOV (*Kolloid Z.*, 1923, **32**, 95—100).—During a repetition of Donau's experiments on the preparation of colloidal solutions of gold (A., 1915, ii, 352) it was found that two types of discharge have to be differentiated. In the first type, where the discharge occurs between two dry electrodes hydrosols are produced because new reducing gases are produced in the vapour above the solution; these gases dissolve

in the solution and reduce the gold chloride. In the second types, the discharge occurs between one dry electrode and the solution or between two moist electrodes, whereby hydrogen peroxide is produced in the solution which reduces the gold chloride. In the portion of the solution which serves as negative pole, coarse violet or blue sols or suspensions are produced whilst the positive portion of the solution contains more or less highly disperse red hydrosols. In both positive and negative parts of the solution acid hydrosols are produced. The polarity of the solution exercises a great influence on the amount of acid in these solutions, which in its turn is determinative of the character of the sol and of its properties. The addition of a solution containing nuclei to the gold chloride solution causes the formation of the sol to take place more easily, reduces the time required for reduction, and produces bright red sols. J. F. S.

Mineralogical Chemistry.

Some New Derivatives of Bituminous Coal. ARCHIBALD R. PEARSON (*J. Soc. Chem. Ind.*, 1923, **42**, 68—72T).—The term "ultrahumin" is suggested for the constituents of coal derived from humified vegetable proteins and celluloses as distinct from resins, waxes, etc. The preparation of α-(pyridine insoluble) and β-, and γ-(pyridine soluble) ultrahumins is described. Oxahumins, produced by oxidation of ultrahumins with fuming sulphuric acid, contain more than 90% of the nitrogen content of the ultrahumins, and, when brominated, take up about one-third of their weight of bromine, forming a series of compounds of approximately constant composition. The brominated products form negative sols in water or alcohol. It is concluded that ultrahumins contain a very stable molecular nucleus including the nitrogen in heterocylic combination. The oxidised nucleus is retained, at least in part, in oxahumins brominated to saturation. J. S. G. T.

The Deposits of Potassium Chloride at Solikamsk. N. S. KURNAKOV, K. F. BELOGLAZOV, and M. K. SCHMATKO (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 122—130).—Samples of rock salt and of sylvine from Solikamsk are described and analysed. The potassium chloride in the former is from 0·26% to 11·9%, and in the latter up to 63·2%. The sylvine is very similar in content and appearance to that found at Stasfurt or Kalusz. Varying small percentages of potassium chloride are found to be present in the mother-liquors from salt works in different parts of Russia. R. T.

Brugnatellite from Monte Ramazzo (Liguria). ETTORE ARTINI (*Atti R. Accad. Lincei*, 1922, [v], **31**, ii, 491—496).—Analysis of brugnatellite from Monte Ramazzo gives the following results:

H_2O.	CO_2.	Fe_2O_3.	MnO.	CaO.	MgO.	Insol. residue.	Total
32·42	8·00	16·12	1·77	1·19	39·13	0·99	99·62

When corrected for the small proportion of extraneous calcium carbonate present, these numbers are in good agreement with those obtained for brugnatellite from Val Malenco (A., 1909, ii, 247) and with the formula proposed by the author, the slight excess of ferric oxide probably existing in the free state as a product of alteration. The results also render evident the distinction between this mineral and pyroaurite, this being borne out by physical differences (cf. Foshag, A., 1920, ii, 765). The brucite from which this brugnatellite is derived by epigenesis contains: H_2O, 30·37; FeO, 1·37; MnO, 0·38; MgO, 67·96; insoluble residue, 0·10; total, 100·18. If these numbers are corrected for the insoluble matter and the FeO and MnO are replaced by MgO, they correspond closely with the composition of $Mg(OH)_2$. T. H. P.

Chemical and Optical Study of the Axinite of Prali (Valle della Germanasca). E. GRILL (*Atti R. Accad. Lincei*, 1922, [v], 31, ii, 521—524).—This axinite, *d* 3·314, occurring as a pale, violet-red vein in a mass of erratic gneiss, has the composition:

SiO_2.	TiO_2.	B_2O_3.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.
41·26	nil	4·70	18·74	2·02	6·11	4·43	1·75

CaO.	H_2O (−110°).	H_2O (+110°).	F.	Total.
19·52	0·46	1·25	trace	100·24

These figures correspond with the formula,

$$H_2O,8(Ca,Fe,Mn,Mg)O,3(Al,Fe)_2O_3,B_2O_3,10SiO_2,$$

which contains 1 mol. of water less than that established by Whitfield (A., 1888, 347) and is not reducible to that of an orthosilicate (cf. Ford, A., 1903, ii, 436). T. H. P.

Analytical Chemistry.

Spectroscopic Methods of Analytical Chemistry. C. AUER-WELSBACH (*Monatsh.*, 1923, 43, 387—403).—A survey of the actual experimental methods employed by the author in carrying out analyses with the aid of spark spectra. Photographs of the apparatus used and a chart showing the lines in the spark spectra of a large number of elements are appended. The effect of the presence of alkalis, zinc oxide, etc., on the spark spectrum of platinum is discussed. E. E. T.

The Application of the Quinhydrone instead of the Hydrogen Electrode in the Potentiometric Measurement of Acidity. I. M. KOLTHOFF (*Rec. trav. chim.*, 1923, 42, 186—198; cf. Biilmann, A., 1921, ii, 372).—The quinhydrone electrode gives excellent results in the titration of acid solutions and may replace the hydrogen electrode for that purpose. It is, however, unsuitable for use in alkaline solution if air is not excluded owing to the oxidation of a portion of the quinhydrone to acid. H. J. E.

Estimation of Blood Alkalinity. HANS GOLLWITZER (*Biochem. Z.*, 1923, **134**, 590—600).—The exact gas analysis method of Barcroft has been compared with the titration methods of Rohanyi (*Münch. med. Woch.*, 1920, **67**, 51), and of Van Slyke (A., 1919, ii, 298). The Van Slyke method yields too high and the Rohanyi method too low results. The gas analysis method is much to be preferred to either of the other two. W. O. K.

The Stability of an 0·01N-Sodium Oxalate Solution. EDWARD S. HOPKINS (*Ind. Eng. Chem.*, 1923, **15**, 149).—The addition of 100 c.c. of 1 : 4-sulphuric acid per litre to sodium oxalate solution prevents its deterioration for at least two months, even when the solution is stored in clear glass bottles exposed to daylight. G. F. M.

The Colorimetric Estimation of Water in Absolute Alcohol. I. M. KOLTHOFF (*Pharm. Weekblad*, 1923, **60**, 227—231).—The sensitiveness of methyl-orange to acids is much less in alcohol solutions than in water solutions, diminishing to a minimum for alcohol of about 90% volume strength, and increasing again for alcohols between 90 and 100%. The sensitiveness is determined by the volume of alcoholic hydrogen chloride ($N/10$) required to produce a standard tint with 0·1 c.c. saturated methyl-orange solution in 25 c.c. of the alcohol under examination. A suitable standard is obtained by adding 0·4 c.c. of $N/100$-hydrochloric acid solution to 0·1 c.c. of saturated methyl-orange solution in 25 c.c. of water; a table is given showing for various alcohols between 95 and 99·7% by volume the sensitiveness expressed in quantities of acid required at 15° to produce the standard tint, compared with the quantity used in water, the figure rising from 5·2 for 99·7% alcohol to 126 for 95% alcohol, compared with 1 for water. The influence of temperature is important, a rise causing the colour to change to the alkaline side in water, but having the opposite effect in alcohol. Figures for temperature correction are given. S. I. L.

Detection of Chlorine, Bromine, Iodine, and Silver in a Mixture of Silver Halides. H. SCHMALFUSS (*Z. anal. Chem.*, 1923, **62**, [6], 229—231).—Silver chloride is extracted from the mixture of silver halides by shaking with a 15% solution of ammonium hydrogen carbonate. The presence of the chloride is confirmed by reprecipitation as silver bromide with potassium bromide. The residue is shaken with hydrogen sulphide solution, and the silver precipitated as sulphide, collected, dissolved in nitric acid, and confirmed by precipitation as chloride with hydrochloric acid. Half the filtrate, after the removal of the silver sulphide, is treated with carbon disulphide and sodium nitrite, and concentrated nitric acid added drop by drop. A violet coloration in the carbon disulphide indicates iodine. The remaining half of the filtrate is treated with carbon disulphide and chlorine water; after the iodine has been oxidised to iodic acid, any bromine liberated produces a brown coloration in the carbon disulphide.

Alternatively, the liquor from the first half after the removal of the iodine may be decanted off, more carbon disulphide added, and the bromine liberated with chlorine water. J. B. F.

Apparatus for the Estimation of Halogens in Organic Compounds. K. RÜBKE (*Z. angew Chem.*, 1923, **36**, 156—158; cf. Voigt, A., 1923, ii, 34).—The halogen compound is dissolved in benzaldehyde or, in the case of liquids of high b. p. and of solids, in a mixture of benzaldehyde and alcohol, and the solution burnt in a lamp of about 20 c.c. capacity provided with an asbestos thread as wick. The lamp is surrounded by a glass chimney and the products of combustion pass through two U-tubes containing glass beads. In each U-tube 25 c.c. of $N/50$-potassium hydroxide are placed to absorb the halogen acid produced in the combustion; this is ultimately washed out through taps at the bottom and titrated with standard silver nitrate. Halogen-free air for the combustion, drawn from outside the laboratory by means of a water-pump, passes through a sulphuric acid drier and enters the combustion chimney through a glass tube in which the lamp is loosely held. The current of air should be about 1 litre per minute. In the case of chlorine compounds, the whole of the hydrogen chloride is absorbed in the first U-tube. Hydrogen bromide, however, is not so readily absorbed and part of it is found in the second U-tube. Whilst the method of Voigt (cf. above) is valuable for rapid routine analyses, the present variation is to be preferred where the time involved is of secondary importance. Further, oxy-hydrogen explosions, which can occur if due precautions are not taken in Voigt's method, are impossible in the above. Full working details and a sketch of the apparatus are given. W. T. K. B.

The Titration of Bleaching Powder. I. M. KOLTHOFF (*Pharm. Weekblad*, 1923, **60**, 241—248).—Bunsen's iodine titration in acid solution gives higher results than other methods; this is not due to the presence of chlorate, but to chlorite formed when the solution or the damp solid is kept. Suitable conditions for the titration are given. Penot's direct titration with arsenite and Pontius's iodide method give accurate results for the hypochlorite content; the best conditions are given. In the latter, petrol is suggested as an indicator instead of starch, the first trace of free iodine forming a violet solution in the organic liquid on shaking. S. I. L.

The Detection of Fluorine in Inorganic Fluorides. H. TER MEULEN (*Chem. Weekblad*, 1923, **20**, 59).—In presence of borates, the etching test gives no result, owing to the formation of boron fluoride. If the gas is passed into water, a cloud is formed, which is seen under a lens to consist of fine crystals. S. I. L.

Limit of Sensitiveness of the Acidification Reaction for Thiosulphates. O. HACKL (*Chem. Ztg.*, 1923, **47**, 174).—The limit of sensitiveness of the reaction for the detection of thiosulphates by the precipitation of sulphur on acidification lies

between a content of 0·1 and 0·05 mg, of S_2O_3 per c.c. With the latter concentration, no cloudiness whatever appears, even on boiling or on long keeping, and even with the former concentration and up to 1 mg. of S_2O_3 per c.c. no immediate separation of sulphur occurs in the cold, and only after some minutes at the boiling temperature. G. F. M.

The Reaction of Silver Nitrate with Thiosulphate and its Sensitiveness. O. HACKL (*Chem. Ztg.*, 1923, 47, 210).—The production of a yellow to brown colour when very dilute solutions of a thiosulphate are treated with silver nitrate is a very delicate reaction, as 0·1 mg. of S_2O_3 can thereby be detected in 100 c.c. of water, whereas the acid test (formation of a white sulphur cloud on acidification) will detect 0·1 mg. in 1 c.c. only. A. R. P.

General Method for the Detection of Volatile Acids. G. KARAOGLANOV (*Z. anal. Chem.*, 1923, 62, 217—222).—The salt solution is mixed in a flask with $2N$-acetic acid and a current of an indifferent gas such as air or hydrogen drawn through the solution. The gas is then led through tubes containing reagents sensitive to the acids concerned. The method is applicable to the following volatile acids: hydrogen cyanide, hydrogen sulphide, nitrous acid, sulphurous acid, hypochlorous acid, and carbonic acid, the detection reagents being silver nitrate, lead acetate, diphenylamine, dilute starch-iodide solution, indigo-solution, and barium hydroxide, respectively. Thiosulphuric acid is decomposed by concentrated acetic acid with the precipitation of sulphur, but in dilute acid no decomposition takes place. Ferro- and ferricyanic acids only decompose on long keeping. The remaining acids under these conditions are non-volatile. To detect sulphite in presence of thiosulphate, acetic acid is added of such a strength that no sulphur is precipitated, and the issuing gas passed through starch-iodide solution. To test for *thiosulphite*: To a portion of the clear solution from the flask, sulphuric acid is added; a precipitation of sulphur indicates thiosulphate. If sulphide is also present, the sulphide is precipitated from neutral solution by zinc chloride, the filtrate tested as above, and the precipitate tested separately. Nitrite in presence of nitrate and chlorate, hypochlorite in mixtures of hypochlorite, chlorate and perchlorate, cyanide in presence of chloride, bromide, ferro- and ferri-cyanides can be readily detected, since the remaining acids in each case are not volatile under the conditions of the experiment. To detect two or more volatile acids in the same mixture the gas is passed through the reagents in series. Thus (*a*) for cyanide and sulphite it is passed successively through (i) a nitric acid solution of silver nitrate, (ii) starch-iodide solution. (*b*) For sulphide and cyanide, through (i) an acetic acid solution of lead acetate, (ii) nitric acid solution of silver nitrate. (*c*) For sulphite, cyanide, and carbonate, through (i) a nitric acid solution of silver nitrate, (ii) a weak solution of starch-iodide to detect sulphite, (iii) concentrated iodine solution to retain sulphite, (iv) barium hydroxide solution. (*d*) For cyanide, sulphite, sulphide, thiosulphate, and carbonate, zinc chloride is added to a neutral solu-

tion and the sulphide, cyanide, and carbonate precipitated and filtered off. The filtrate and precipitate are then examined separately as above. As a preliminary experiment in order to determine whether any of the volatile acids are present the gas is passed separately through reagent tubes containing (i) a nitric acid solution of silver nitrate, (ii) barium hydroxide solution, (iii) starch-iodide solution. A turbidity indicates in (i) cyanide, sulphide, or hypochlorite, in (ii) sulphite or carbonate; a blue coloration in (iii) indicates hypochlorite or nitrite. The volatile acids included in this scheme form an analytical group. J. B. F.

Detection of Nitrogen in Mineral and Organic Substances by Microchemical Methods. AL. IONESCU and C. HÂRŞOVESCU (*Bul. Soc. Chim. România*, 1922, **4**, 61—65).—The formation of yellow crystals of ammonium picrate of characteristic appearance when even small traces of ammonia vapour are allowed to impinge on a drop of picromalonic reagent (a saturated solution of picric acid in ethyl malonate) or of an alcoholic solution of picric acid containing 5% of glycerol, on a microscope slide, may be used as a delicate specific test for ammonia nitrogen. With the picromalonic reagent tiny, quadratic crystals are formed, whilst with the alcoholic picric acid larger crystals in the form of more or less elongated yellow prisms are obtained. The latter reagent is the more sensitive owing to the evaporation of the alcohol. The ammonia is generated by heating the substance to be tested with sodium hydroxide solution if inorganic, or with soda-lime if organic. Volatile amines do not give the reaction. G. F. M.

Estimation of Phosphorus. G. E. F. LUNDELL and J. I. HOFFMAN (*Ind. Eng. Chem.*, 1923, **15**, 171—173).—Details are given of the application of the methods described in the first part of this paper (this vol., ii, 85) to the estimation of phosphorus in metallurgical products such as iron, plain carbon steel, alloy steel, and bronze. The reduction method is slightly more trustworthy with solutions which do not contain interfering elements than the alkalimetric method, but the advantage does not outweigh its inconvenience, and probably vanishes with phosphomolybdate obtained in the presence of such reducible substances as titanium, arsenic, or vanadium. The alkalimetric method yields under severe conditions values sufficiently accurate for technical purposes provided attention is paid to the temperature at which precipitation is effected. The direct precipitation of phosphorus as phosphomolybdate in bronze assays has not hitherto been recommended, but by following the method here described, provided a clear solution can be obtained in the amount of mixed nitric and hydrochloric acids specified, better recovery of the phosphorus has actually been obtained than by the widely-used Oettel method. 1—3 G. of the bronze are dissolved in a mixture of 15 c.c. of nitric acid and 5 c.c. of hydrochloric acid, 15 c.c. of water are added, and after digesting at 80° for ten minutes and diluting to 50 c.c., 100 c.c. of the molybdate reagent are added, and the mixture is kept for four to six hours. The precipitate is then collected, dissolved in 20 c.c. of ammonia

containing 2 g. of citric acid, and the ammoniacal solution treated as previously described (*loc. cit.*). Tungsten steel must also be dissolved in a nitro-hydrochloric acid mixture. G. F. M.

Estimation of Phosphorus in Vanadium Ores. F. W. KRIESEL (*Chem. Ztg.*, 1923, **47**, 177—178).—Precipitation of phosphoric acid in the presence of relatively large amounts of vanadic acid by means of ammonium molybdate yields an orange-brown precipitate containing much vanadic acid. Treadwell's modification involving reduction of the vanadium to vanadyl sulphate also gives high results. Satisfactory results may be obtained by removing the vanadium as vanadyl ferrocyanide after first effecting a concentration and partial separation of the phosphoric acid by boiling the solution with nitric acid and tin. The precipitate contains all the phosphorus and some vanadium; it is fused with potassium cyanide to remove tin and arsenic and the solution of the fused mass is boiled with hydrochloric acid to expel hydrocyanic acid, then with potassium ferrocyanide to precipitate the remaining vanadium. The filtrate is treated with alum and ammonia to separate the phosphoric acid from chlorides and ferrocyanides, the precipitate is dissolved in nitric acid, and the solution treated with molybdate mixture in the usual way (cf. *J.S.C.I.*, 1923, April). A. R. P.

Valuation of Insoluble Phosphates by means of a Modified Citric Acid Test. G. S. ROBERTSON and F. DICKINSON (*J. Soc. Chem. Ind.*, 1923, **42**, 59—62T).—The authors contend that the respective values of phosphatic fertilisers may be determined by a modification of the solubility test proposed by Wagner. For this purpose, they propose that the solubility be determined by shaking 1 g. of the phosphate (in place of 5 g. proposed by Wagner) with 500 c.c. of 2% citric acid solution for half an hour in a shaker making 30 revolutions per minute. Results of field tests are given in support of the contention. J. S. G. T.

Electrolytic Apparatus for the Estimation of Arsenic. G. W. MONIER-WILLIAMS (*Analyst*, 1923, **48**, 112—114).—The apparatus is a modification of that described by Sand and Hackford (T., 1904, **85**, 1018), lead electrodes being used. The walls of the porous pot are little more than 1 mm. thick. The anode is a strip of lead foil and the cathode a disk of the same material about 2·5 cm. in diameter. The central glass vessel and the tap funnel are blown in one piece and the calcium chloride tube is connected by a ground glass joint. The hard glass tube for the reception of the arsenic mirror is 2 mm. in diameter and is connected with the apparatus by a short piece of caoutchouc tubing. A piece of metal gauze is wrapped round the part of the tube exposed to the flame and a sharper arsenic mirror is obtained by wrapping a small piece of filter-paper round the tube, with its end dipping into water. The current used is 5—6 amperes, the potential difference between the electrodes being 7—9 volts. Foodstuffs of the most varied character can be tested without preliminary treat-

ment. Large amounts of phosphoric acid or phosphates appear to inhibit the formation of arsine. Iron also acts as an inhibiting agent when no organic matter is present. The small quantities of phosphates and iron present in many foodstuffs do not appear to have any effect. The electrolytic method is sensitive to 0·001 mg. of arsenious oxide, and to a great extent eliminates the personal equation. H. C. R.

Potentiometric Titration of Arsenic and Antimony. EDUARD ZINTL and HERMANN WATTENBERG (*Ber.*, 1923, **56**, [*B*], 472—480).—Tervalent arsenic and antimony can be readily estimated by titration with standard potassium bromate in hydrochloric acid solution, the end-point being determined potentiometrically (cf. Zintl and Wattenberg, A., 1922, ii, 871).

In the case of tervalent arsenic, the end-point indicated potentiometrically is identical with that given by methyl-orange if the concentration of hydrochloric acid is below 10%. The potentiometric method has, however, the advantage that the proximity to the end-point is much more distinctly indicated and the titration can therefore be more rapidly performed.

Tervalent antimony may be estimated in cold solution in the same manner as arsenic. [Test analyses indicate that the value, 120·2, usually adopted for the atomic weight of antimony is more than 1% low, but are in harmony with the datum, 121·77, of Willard and McAlpine (A., 1921, ii, 405).] The titration can be equally effected in hot solution if atmospheric oxidation is avoided by rapid manipulation.

Reduction of quinquevalent antimony is effected by the action of titanium trichloride solution in the presence of a little copper sulphate on the nearly boiling antimony solution, which must contain about 5% of hydrochloric acid. The end-point of the reduction is determined potentiometrically, after which the titration with bromate is effected as usual. Alternatively, the antimony solution, containing at least 5% of free hydrochloric acid, is heated nearly to boiling and treated with ten drops of phosphotungstic acid (10%). Titanium trichloride is added with constant shaking until a marked blue colour is developed which does not disappear after two minutes. Three drops of copper sulphate solution (1%) are added as catalyst, and the solution is shaken and exposed to air as much as possible, whereon the blue colour disappears within one to two minutes. The solution is immediately titrated with bromate in the presence of methyl-orange. The presence of stannic salts does not cause complications in this or the potentiometric estimation of antimony.

The reduction of quinquevalent arsenic is effected with great difficulty by stannous chloride, chromous chloride, or titanium trichloride. It is therefore readily possible to estimate antimony by titration in the presence of quinquevalent arsenic; in this case, the potentiometric method must be used, since the presence of phosphotungstic acid causes the reduction of arsenic acid.

If arsenic and antimony are present entirely in the tervalent

condition, they may be estimated in a single solution. Their sum is first estimated by titration with bromate solution, and subsequently the antimony is determined alone after reduction with titanium chloride under potentiometric control.

Preliminary experiments show that thallium, sulphurous acid, potassium ferrocyanide, and hydrazine can also be estimated potentiometrically. H. W.

The Estimation and Separation of Arsenic, Antimony, and Tin. K. K. JÄRVINEN (*Z. anal. Chem.*, 1923, **62**, 184—204).—After describing experiments in which the accuracy of the bromate method for the titration of arsenious and antimonious chlorides is proved, it is shown that the completeness of the reduction of stannic chloride by iron depends on the complete exclusion of air from the apparatus until the solution is quite cold and on the use of sufficient iron, at least 6 g. of ferrum redactum per 100 c.c. of solution being required. The most satisfactory reducing and volatilising agents for use in the separation of arsenic from antimony and tin by distillation from a chloride solution were found to be potassium iodide and a mixture of potassium bromide and sodium sulphite. In the latter case, the distilling flask must be fitted with a 3-bulb Young's stillhead in order to avoid any antimony passing over towards the end of the distillation. The complete separation of antimony from tin by precipitation with metallic iron is extremely difficult, as the precipitate almost invariably contains tin and if an attempt to remove this by prolonged digestion of the precipitate in the solution is made a certain amount of antimony dissolves. However, addition of a further small quantity of iron and filtration of the solution before all the iron is dissolved yields a precipitate free from tin, but containing iron and not suitable for titration with bromate. It is rinsed back into the beaker, the residue on the paper dissolved in hydrochloric acid with a few mg. of potassium chlorate, and the solution treated with twice its bulk of hydrogen sulphide water. The precipitate is collected, washed, and dissolved in nitric and sulphuric acids. The solution, including the filter-paper, is heated in a Kjeldahl flask until colourless, 1 g. of sodium thiosulphate is added, and the heating continued until all the sulphur has disappeared. The mass is dissolved in water and titrated with potassium bromate. The filtrate from the first antimony precipitate is reduced with iron and titrated for tin as usual. A. R. P.

Apparatus for Use in the Combustion Analysis of Volatile Hygroscopic Liquids. JOHN BALDWIN SHOESMITH (*J. Soc. Chem. Ind.*, 1923, **42**, 57—58T).—The apparatus consists of a capillary bulb tube which is connected by a capillary opening with a second and somewhat larger bulb; the latter serves as an air reservoir. After the sample has been introduced into the capillary bulb, the capillary is sealed and the end inserted into a short piece of glass tubing which is constricted at its middle. The whole is placed in the combustion tube and the capillary is broken against the constriction in the glass tubing by applying pressure to the

latter. The sample is expelled from the capillary bulb by the expansion of the air in the second bulb as this becomes heated.

W. P. S.

Estimation of Carbon Dioxide in Carbonates. K. K. Järvinen and O. Sumelius (*Z. anal. Chem.*, 1923, 62, 222—229).—For carbonates associated with starch, as in baking powders, the substance containing 0·3—0·6 g. of carbon dioxide is introduced into a 200 c.c. flask, fitted with a dropping funnel, and connected to a ten-bulbed absorption tube containing 50 c.c. of *N*-sodium hydroxide, and this in turn connected to a guard tube also containing sodium hydroxide. The rate of evolution should be one to two bubbles per second. Then air free from carbon dioxide is slowly passed through the contents of the flask at the ordinary temperature for two hours to expel the last traces of carbon dioxide. The solution from the bulbs is treated with 50 c.c. of barium chloride solution, then titrated with *N*-hydrochloric acid with phenolphthalein as indicator. In cases in which the solution may be boiled, the substance, together with 100 c.c. of water, is placed in a 300—400 c.c. Kjeldahl flask, through the stopper of which passes a 40 cm. dropping funnel; the stem is filled with water and the funnel closed with a well-fitting stopper to prevent regurgitation by the back pressure due to boiling. By means of a 50 cm. tube, drawn out for 2 cm. at the lower end, the flask is connected to the bottom of an 80 cm. burette tube, the two tubes being inclined at about 30°. The top of the burette is fitted with a soda-lime tube. Fifty c.c. of *N*-sodium hydroxide are put into the burette, lacmoid and pumice added to the flask, and the contents boiled to expel all the air. Keeping a similar rate of boiling, 25 c.c. of 2*N*-hydrochloric acid are added at a rate of one to two drops per second, and when all the acid has been added, the liquid is boiled for two to three minutes. The contents of the burette are then treated with barium chloride, and titrated as already described. The operation takes half an hour and is very accurate.

J. B. F.

Rapid Estimation of Potassium in Acid-insoluble Silicates. Manuel M. Green (*Ind. Eng. Chem.*, 1923, **15**, 163).—The method depends on the assumption that all metals except potassium form perchlorates soluble in 97% alcohol; 0·15—0·35 g. of the sample is weighed out into a platinum crucible, 1·5 c.c. of 2*N*-perchloric acid and 3—4 c.c. of 48% hydrofluoric acid are added, and evaporated until fumes of perchloric acid are given off. The crucible is cooled and two-thirds filled with water, heated to boiling, filtered, and thoroughly washed with hot water, the filtrate and washings being run into a platinum dish. The liquid is evaporated until fumes of perchloric acid are evolved, cooled, and 25 c.c. of 97% alcohol are added. The residue is broken up and filtered on an untared Gooch crucible and thoroughly washed with the perchloric acid-alcohol mixture. The asbestos mat and precipitate are transferred to a filter, thoroughly washed with hot water, and filtered into a platinum dish. 0·5—1·0 C.c. of 2 *N*-perchloric

acid is added and the liquid evaporated until fumes appear, cooled, 25 c.c. of 97% alcohol are added, the precipitate is broken up and filtered on a tared Gooch crucible, washed with alcohol containing perchloric acid, and dried to constant weight at 110°. The method is accurate to ±0·2%, and the estimation requires two to three hours. H. C. R.

The Alkali Content of Blood and Cerebrospinal Fluid. A New Method for the Estimation of Sodium. M. RICHTER-QUITTNER (*Biochem. Z.*, 1922, **133**, 417—432).—A method for the estimation of sodium in the blood is described, based on ultra-filtration followed by precipitation of the sodium by potassium pyroantimonate. Venous stasis, and likewise the removal of carbon dioxide has no influence on the sodium content. Under normal conditions, the corpuscles contain no sodium. W. O. K.

Isatin as a Microchemical Reagent. J. B. MENKE (*Rec. trav. chim.*, 1923, **42**, 199—203).—The silver and cuprous salts of isatoic acid have crystalline forms which are easily recognisable. They are precipitated on addition of a solution of the metallic salt to a 5% solution of ammonia in which isatin has been dissolved. The corresponding silver ammonium compound is also noted.

H. J. E.

The Application of Conductometric Titrations to Precipitation Analysis. VIII. Conductometric Titrations with Lithium Oxalate. I. M. KOLTHOFF (*Z. anal. Chem.*, 1923, 62, 161—177).—Silver, lead, and copper may be accurately titrated conductometrically with lithium oxalate, the end-point in each case being accompanied by a very abrupt change in the conductivity of the solution. Cadmium and zinc salts give much less trustworthy results, which become very erratic if alcohol is added. Nickel-, cobalt-, manganese-, and ferrous-ions appear to form complexes on the addition of the oxalate so that two deflections, neither of which is very definite, occur in the conductivity curve, the first corresponding with the addition of half the oxalate required to form the normal salt. Magnesium gives low results owing to the appreciable solubility of magnesium oxalate and its tendency to form complexes and supersaturated solutions. Barium, strontium, and calcium in neutral solutions may be satisfactorily estimated by the process; calcium also gives good results in ammoniacal solutions and at extreme dilutions, provided that 30% of alcohol is present. The presence of magnesium in the calcium solution gives very high results, but if a great preponderance of calcium ions is present the sum of the two metals is accurately estimated by titration conductometrically with lithium oxalate, so that this process may be applied to the determination of the hardness of potable water. A. R. P.

Application of Conductometric Methods to Precipitation Analysis. X. Conductometric Titrations with Potassium Ferricyanide. I. M. KOLTHOFF (*Z. anal. Chem.*, 1923, **62**, 214—215).—On account of the great mobility of the potassium-ions the

different points of inflection of the conductometric curves with potassium ferricyanide are not sharp and as an analytical reagent the latter finds only a little application. Lithium ferricyanide would be more suitable. Silver forms a red-coloured salt, $Ag_3Fe(CN)_6$. The conductometric curve resembles that for potassium, being almost horizontal up to the point of inflection. Copper and cadmium can be accurately estimated. Lead does not form a precipitate with potassium ferricyanide and the conductometric curve is a straight line. Cobalt forms a blue precipitate, $Co_3[Fe(CN)_6]_2$. A very dilute solution of cobalt containing 10 mg. of cobalt per litre gives a distinct red coloration. Nickel gives a faintly orange-coloured precipitate with the reagent. Nickel and cobalt are accurately estimated by this method. Manganese gives irregular results. Zinc also is not accurately estimated. With the exception of those of zinc and manganese the salts are of normal composition.
J. B. F.

Application of Conductometric Methods to Precipitation Analysis. XI. Conductometric Titrations with Sodium Nitroprusside. I. M. KOLTHOFF (*Z. anal. Chem.*, 1923, **62**, 216—217).—Various metals give with sodium nitroprusside a precipitate of normal composition. Only silver is accurately estimated by conductometric titration.
J. B. F.

The Volumetric Estimation of Calcium. A. VÜRTHEIM and H. G. C. VAN BERS (*Chem. Weekblad*, 1923, **20**, 68).—An answer to the criticisms of Grossfeld (this vol., ii, 183) on the method put forward by the authors (A., 1922, ii, 869). Neutralisation with sodium hydroxide in the cold is more likely to cause precipitation of phosphate than addition of ammonia drop by drop at the boiling point.
S. I. L.

Method for the Quantitative Separation of Glucinum and Uranium. PAUL H. M.-P. BRINTON and REUBEN B. ELLESTAD (*J. Amer. Chem. Soc.*, 1923, **45**, 395—398).—The quantitative separation and estimation of uranium and glucinum in mixtures of compounds of the two elements has been investigated and the following method evolved. To the hydrochloric acid solution about 5 g. of ammonium chloride and 5 g. of hydroxylamine hydrochloride are added, followed by a concentrated solution of ammonium carbonate, which is added until the precipitate at first formed is entirely redissolved. The solution is heated to boiling and the boiling continued for one minute after the appearance of a heavy precipitate of basic carbonate. The precipitate is filtered immediately and thoroughly washed with cold water. This basic carbonate precipitate is free from uranium. It is set aside to be ignited with the small amount of glucinum hydroxide which is to be separated from the filtrate. The filtrate is acidified with hydrochloric acid and boiled to expel carbon dioxide, then after the addition of 1 g. of hydroxylamine hydrochloride a slight excess of ammonia is added to the cold solution and the small precipitate of glucinum hydroxide is filtered and washed with 2% ammonium nitrate solution to which

have been added a few crystals of hydroxylamine hydrochloride and sufficient ammonia to make the solution faintly alkaline. The combined glucinum precipitates are ignited and weighed as oxide. The filtrate is acidified with hydrochloric acid and the hydroxylamine oxidised either by adding 75—100 c.c. of 3% hydrogen peroxide solution and boiling until the evolution of oxygen ceases, or by adding solid sodium or potassium bromate with constant stirring until the solution assumes an intense colour of bromine. The oxidised solution is heated nearly to the boiling point and a slight excess of ammonia is added with constant stirring. After settling, the ammonium uranate is filtered and washed with 2% ammonium nitrate solution which contains a little free ammonia. The precipitate is ignited and weighed as U_3O_8. The method is good and gives trustworthy and accurate results. J. F. S.

A Rapid Volumetric Method for the Estimation of Magnesia in Carbonate Rocks. H. R. BRANDENBERG and A. H. AVAKIAN (*Concrete* [*Mill Section*], 1922, 21, 78).—One g. of the sample is treated in an Erlenmeyer flask fitted with a reflux condenser with 60 c.c. of 0·4*N*-hydrochloric acid containing 2 c.c. of an alcoholic solution of phenolphthalein per litre. After boiling and cooling, the excess of hydrochloric acid is titrated with 0·4*N*-sodium hydroxide, the first pale pink colour being taken as the end-point. The mixture is again boiled, 1·5 g. of sodium oxalate and an excess of 0·4*N*-sodium hydroxide are added, and boiling is continued for a few minutes. The liquid is then cooled, diluted to 200 c.c., filtered, and 100 c.c. of the filtrate are titrated with 0·4*N*-hydrochloric acid. It is assumed that the loss of acidity in dissolving the substance is due entirely to the presence of calcium and magnesium carbonates, and that the final precipitate consists of calcium oxalate and magnesium hydroxide.

CHEMICAL ABSTRACTS.

The Alkalimetric Estimation of Magnesium and Calcium Salts. RICHARD WILLSTÄTTER and ERNST WALDSCHMIDT-LEITZ (*Ber.*, 1923, **56**, [*B*], 488—491).—The methods depend on the observation that the solubility of magnesium and calcium hydroxides can be so depressed by the use of suitable solvents that the substances do not affect appropriate indicators.

The aqueous solution of a magnesium salt is gradually treated with an excess of alkali hydroxide solution (*N*/10—*N*/1) and so much ethyl alcohol is added that the concentration of the latter is 66—75%. After ten to fifteen minutes, the excess of alkali is titrated with hydrochloric acid in the presence of thymolphthalein (about 10 drops of a 0·5% alcoholic solution are used for each 100 c.c. of liquid); phenolphthalein cannot be employed. Ethyl alcohol may be replaced by methyl alcohol the suitable concentration of which is also 66—75%; in this case, the titration is complicated by the adsorption of the indicator by the precipitated magnesium hydroxide and the method is only suitable in certain circumstances (see later).

Aqueous alcoholic solutions are unsuitable for the estimation of

calcium, which is performed as follows. An excess of alkali hydroxide ($N/10$ to $N/1$) is added drop by drop to the aqueous solution of the calcium salt, which is subsequently treated with neutral acetone until the concentration of the latter is 85—90%. After fifteen minutes, the excess of alkali is titrated in the presence of thymolphthalein (10 drops in 200 c.c. of liquid) until the blue colour permanently disappears. Towards the end of the titration the colour is temporarily discharged, but returns as the adsorbed alkali hydroxide again passes into solution.

When magnesium and calcium hydroxides are simultaneously present, the sum of the bases is estimated in 90% acetone. Magnesium alone is estimated in 66% methyl or ethyl alcohol. If calcium is present in relatively small amount, ethyl alcohol is to be preferred on account of the sharper end-point. If, however, calcium is present in equal or excess quantity, the method is inaccurate, since the magnesium hydroxide carries down and retains small amounts of calcium hydroxide. In these circumstances, methyl alcohol (66—70%), in which calcium hydroxide is more freely soluble, must be used; the end-point of the titration is shown by the first complete disappearance of the blue colour of the thymolphthalein; no attention is paid to the bluish-violet coloration which gradually develops in the magnesium hydroxide.

If iron is also present,* as in the analysis of dolomite, it is either precipitated with the aluminium hydroxide and the ammonium salt is expelled or is completely converted into the ferrous state by means of sulphur dioxide. Ferrous hydroxide behaves like magnesium hydroxide in the presence of ethyl alcohol or acetone and is estimated simultaneously; it is separately determined by titration with potassium permanganate. H. W.

The Estimation of Zinc in Minerals. ET. OLIVIER (*Mon. Sci.*, 1923, **13**, 31—35).—About 1·5 g. of the mineral, ground to pass an 80-mesh sieve, is dissolved in 20—25 c.c. of hydrochloric acid with subsequent addition of 10 c.c. of nitric acid. After evaporation to dryness, and dehydration of silica, the residue is taken up with 5 c.c. hydrochloric acid and diluted with 30 c.c. of warm water. Saturated hydrogen sulphide solution is added until the volume amounts to about 125 c.c. The precipitated lead, copper, antimony, arsenic, and cadmium sulphides are filtered, and washed with about 150 c.c. of warm water containing 5 c.c. of hydrochloric acid and a few c.c. of hydrogen sulphide solution. The filtrate is boiled to expel hydrogen sulphide, and brought to a volume of about 200 c.c. Ten c.c. of nitric acid, and, after cooling, 2—20 c.c. of hydrogen peroxide or 5—50 c.c. of bromine water (according to the amount of manganese present), are added to the solution. Iron, aluminium, and manganese are precipitated by the addition of 60 c.c. of ammonia, the liquid being allowed to remain over-night with free access to the air. The solution is filtered and titrated with sodium sulphide solution, using lead test-paper as an outside indicator. Titrations are compared with those of a standard zinc solution, which is prepared

by a similar process to that to which the mineral has been subjected. The same tint of sulphide stain on the test-paper should be adopted as the end-point in each case, and this should be further confirmed by the addition of (say) 0·2 and 0·5 c.c. of sulphide solution, which should produce similar intensifications of the stain in both cases.

A. G. P.

Electrometric Estimation of Zinc by means of Silver Nitrate. ERICH MÜLLER and ALFRED ADAM (*Z. Elektrochem.*, 1923, **29**, 49—53).—Using much the same method as was previously employed for the estimation of nickel and cobalt (A., 1922, ii, 875) the authors now show that zinc may be estimated electrometrically. The determination is carried out by treating 10 c.c. of the zinc solution with an excess of potassium cyanide solution and titrating the excess of potassium cyanide with $N/10$-silver nitrate solution, using a silver wire as indicator electrode. It is also possible to determine simultaneously the amount of silver which may be present with the zinc by the same process. Cadmium, lead, and copper cannot be estimated by this method.

J. F. S.

Application of Conductometric Methods to Precipitation Analysis. IX. Conductometric Titrations with Potassium Ferrocyanide. I. M. KOLTHOFF (*Z. anal. Chem.*, 1923, **62**, 209—214).—Lead can be accurately estimated by conductometric titration with potassium ferrocyanide, since it forms only the normal salt. Zinc may also be accurately estimated in weak ammoniacal solution; stronger ammoniacal solutions require less reagent. A mixture made up of 20 c.c., 0·05 M of zinc sulphate, 20 c.c. of water, and 2·5 c.c. of a 10% solution of ammonia required 1·99 c.c. of 0·25 M reagent at the point of inflection, whereas with 18 c.c. of the ammonia solution this point was reached with 1·78 c.c. of the reagent, 2·00 c.c. being the calculated value. In the absence of ammonia, two points of inflection occur, the first corresponding with the normal salt, $Zn_2Fe(CN)_6$, and the second with

$$K_2Zn_3[Fe(CN)_6]_2.$$

Silver, copper, cadmium, manganese, nickel, and cobalt first give rise to a normal salt, which combines with a further quantity of reagent to form double salts. Silver gives a second point of inflection corresponding approximately with $KAg_3Fe(CN)_6$, copper and cadmium at $K_2Cu_3[Fe(CN)_6]_2$ and $K_2Cd_3[Fe(CN)_6]_2$, respectively. Copper gives a third point at $K_4Cu_4[Fe(CN)_6]_3$. Manganese, nickel, and cobalt behave similarly to copper, but with the formation of a further point corresponding with a composition of the type $[3K_4Fe(CN)_6+4MnFe(CN)_6]$.

J. B. F.

Electro-analytical Methods for the Estimation of Metals in Hydrochloric Acid Solution. ANNA J. ENGELENBURG (*Z. anal. Chem.*, 1923, **62**, 257—284).—The methods proposed by Schoch and Brown (A., 1913, ii, 794) for the electrodeposition of tin, copper, antimony bismuth, lead, and cadmium from chloride solutions in the presence of hydroxylamine hydrochloride have

been further studied and modifications in the temperature, quantity of hydroxylamine hydrochloride added, and the current used are suggested. Application of the results to the separation of certain of the above metals from one another are also suggested.

The following new processes are described. Cadmium is deposited from a solution containing 10 c.c. of hydrochloric acid in 200 c.c. bulk by electrolysing for twenty minutes at 1 ampere, then adding 20 g. of ammonium oxalate and 10—20 g. of oxalic acid and continuing the electrolysis for a further forty minutes at 1·2 amperes. Zinc is estimated by electrolysis of a solution containing 1·5 c.c. of hydrochloric acid and 2 g. of hydroxylamine hydrochloride in 200 c.c.; the temperature is maintained at 18° and the current increased slowly from 4 to 8 amperes. In all the above processes hydrazine sulphate may be used instead of hydroxylamine hydrochloride, and in the case of copper 0·1—0·2 g. of ammonium persulphate in place of either of the other two reagents gives a more firmly adherent and smoother deposit. A mixture of 0·4 g. of ammonium persulphate and 0·5 g. of hydroxylamine hydrochloride in 150 c.c. of a tin solution containing 12 c.c. of hydrochloric acid improves the nature of the tin deposit. By measuring the cathode potentials of a solution containing the above metals, the presence or absence of each in the solution may be ascertained, by the potential changes as each metal is deposited. A. R. P.

Lead. II. Electrolytic Estimation of Lead in Biological Material. A. S. MINOT (*J. Biol. Chem.*, 1923, **55**, 1—8).—The method described by Denis and Minot (A., 1919, ii, 372) is inaccurate and is, in fact, untrustworthy even as a qualitative test for lead. This is due partly to the presence of manganese and partly to other factors. Fairhall's method (A., 1922, ii, 659), however, gives accurate results. E. S.

The Carrying Down of Acids by Alumina Precipitates. ANDRÉ CHARRIOU (*Compt. rend.*, 1923, **176**, 679—682).—When alumina is precipitated by ammonia in presence of an alkali chromate, the precipitate remains yellow, even after prolonged washing with boiling water. The alkali metal could not be detected in the precipitate, and it is therefore only the acid which is carried down by the alumina, and it probably forms a layer of aluminium chromate on the alumina, which may constitute anything from 1—7% of the total weight. A similar absorption of chromic acid occurs when precipitated aluminium hydroxide is placed in contact with potassium chromate solutions. The precipitate cannot be freed from chromic acid by washing with ammonium nitrate, chloride, or acetate solutions, but when the alumina is precipitated with ammonium hydrogen carbonate or precipitated with ammonia and washed subsequently with 5% ammonium hydrogen carbonate solution, it is obtained perfectly colourless and free from chromate. A similar result is obtained with lithium or sodium carbonate, or with ammonium phosphate, the carbonic or phosphoric acid apparently displacing the chromic acid, and taking its place. In

analysis, it is sufficient, therefore, to wash the alumina with 5% ammonium hydrogen carbonate solution in order to eliminate chromic acid, the carbonic acid and ammonium salts remaining in the precipitate being subsequently removed during the calcination. G. F. M.

Qualitative Analysis of the Iron Group. RALPH W. HUFFERD (*J. Amer. Chem. Soc.*, 1923, **45**, 438—439).—A modified method of treating the iron group precipitate in qualitative analysis is described. The precipitate is treated with a large excess of sodium hydroxide to remove the aluminium, zinc, and chromium. The precipitate is treated directly with nitric acid and potassium chlorate to remove the manganese. Iron is removed by adding a large excess of ammonia. The filtrate from the iron precipitate is evaporated until it has only a faint odour of ammonia and one-fifth of the solution treated with dimethyl-glyoxime to test for nickel. The remainder of the solution is evaporated to a syrup, treated with sufficient water to dissolve the salts, and tested for cobalt by adding 3 c.c. of 10% potassium thiocyanate followed by 3 c.c. of a mixture of amyl alcohol and ether (1 : 3). In the presence of cobalt the solution becomes bluish-green; if the colour is indistinct the careful addition of a few drops of 12*N*-hydrochloric acid will develop the colour if cobalt is present. In the absence of cobalt, the colour of the ether layer will be straw-coloured or colourless. J. F. S.

Volumetric Estimation of Tervalent Iron and of Copper in the Presence of Iron. FRIEDRICH L. HAHN and HEINRICH WINDISCH (*Ber.*, 1923, **56**, [*B*], 598—601).—The iodometric estimation of ferric salts involves a large expenditure of time and iodide, since the reaction $Fe^{\cdot\cdot\cdot}+I' \rightleftharpoons Fe^{\cdot\cdot}+I$ is reversible, and dissociation only occurs slowly when the liberated iodine is removed. Since, however, cupric salts are instantaneously reduced by iodides to iodine and cuprous salts and the latter convert ferric salts into ferrous compounds, it is possible to catalyse the action of ferric salts and iodides by the addition of a small amount of cuprous compounds to such an extent that the titration can be performed immediately and in the presence of only a small quantity of iodide. The use of isolated cuprous iodide is unnecessary. It is sufficient if the potassium iodide solution is treated with a little copper sulphate and starch and subsequently with sodium thiosulphate until the blue colour is just discharged; the suspension is added to the solution of the ferric salt and the liberated iodine is immediately titrated with thiosulphate. The method is considered to be the most convenient and trustworthy for the standardisation of thiosulphate solutions.

It appears, therefore, that the sum of copper and iron can be immediately estimated by titration in mixtures of ferric and cupric salts. The action of the iron can be eliminated by the addition of a solution of sodium phosphate, which has been treated with phosphoric acid until it decolorises *p*-nitrophenol, to the

neutral or faintly acid solution. If the ferric solution is strongly acidic, it may be partly neutralised, phosphate without phosphoric acid may be used, or a larger proportion of the mixture may be employed. It is sufficient if two molecular proportions of phosphate are added for each molecule of ferric salt. It is immaterial whether ferric phosphate is precipitated or not. The estimation of copper is not influenced by the addition of phosphate. H. W.

Estimation of Bismuth as Phosphate and Its Separation from Lead, Copper, and Cadmium. G. LUFF (*Chem. Ztg.*, 1923, 47, 133—134).—The precipitation of bismuth as phosphate from a slightly acid solution of the nitrate serves to separate it from copper, lead, and cadmium if the operation is conducted as follows. The nitric acid solution of the metals is exactly neutralised with ammonia, using methyl-orange as indicator, 4 c.c. of nitric acid are added, and the bismuth is precipitated by the addition, drop by drop, to the boiling solution of a solution of 1 g. of ammonium phosphate in 40 c.c. of water and 2 c.c. of nitric acid. The dense, crystalline precipitate of bismuth phosphate is collected, washed with hot water, ignited wet together with the filter-paper, and weighed. If the filtrate contains only cadmium, this is precipitated as sulphide after the addition of an excess of ammonium acetate and the sulphide is dissolved in hydrochloric acid. The solution is rendered neutral to methyl-orange by the addition of potassium carbonate and the cadmium precipitated by a large excess of diammonium hydrogen phosphate. The precipitated cadmium ammonium phosphate is collected on a filter, washed first with dilute ammonium phosphate solution, then with 60% alcohol, ignited, and weighed as pyrophosphate (cf. Schoeller and Waterhouse, A., 1921, ii, 195). A. R. P.

New Compounds of Platinum, Palladium, Iridium, and Rhodium, and a New Method for their Estimation. W. N. IVANOV (*Chem. Ztg.*, 1923, 47, 209—210).—When 0·25% solutions of potassium chloroplatinite and sodium thiocyanate are mixed and left for five to six hours at the ordinary temperature, then shaken with 50 g. of ammonium nitrate or sulphate per litre, a light brown, flocculent precipitate of platinous thiocyanate is produced. The precipitate is soluble in aqua regia and in potassium cyanide solution, but not in single acids or alkalis. If the precipitation is carried out in boiling solutions, a black, flocculent precipitate having the composition $Pt_4(OH)_4S(CS{\cdot}NH_2)_2$ is obtained. On ignition, a residue of platinum is left so that the compound is suitable for use in the estimation of platinum. Under similar conditions, palladium gives a precipitate of $Pd_3S_2(CS{\cdot}NH_2)_2$, which on ignition leaves a very fusible residue of Pd_3S which is slowly transformed, after prolonged heating, into the metal. Rhodium also gives a black precipitate the composition of which, however, was not ascertained. On ignition it yields metallic rhodium. Iridium is incompletely precipitated as a flocculent, yellow compound. A. R. P.

The Detection of Methyl Alcohol in Ethyl Alcohol. H. W. van Urk (*Pharm. Weekblad*, 1923, **60**, 273—276).—Distillation should be carried out as recommended in the German official method, the first 10 c.c. from 100 c.c. of the sample being again distilled and the first 1 c.c. taken. Oxidation may be conveniently carried out by means of the copper spiral, and formaldehyde detected by Denigès's method; a positive result should be confirmed by the morphine-sulphuric acid test. S. I. L.

Characterisation of the Alkylglycerols. Raymond Delaby (*Compt. rend.*, 1923, **176**, 396—399; cf. this vol., i, 84, 85).—The author has tested the reactions described by Denigès ("Précis de Chimie analytique," 1920, 151) for glycerol with methyl-, ethyl-, propyl-, and butyl-glycerols to see how far they are specific. After oxidation with bromine, of the colours obtained in the presence of sulphuric acid with certain alkaloids or phenols only that with codeine, namely, a blue colour, is specific to glycerol. Similarly, if potassium bromide is added to the oxidation products before the sulphuric acid and then the colour tests described are applied, only the colour, blue, with guaiacol serves to distinguish glycerol from its homologues. If the osazone test is applied to the oxidation products, the osazone from methylglycerol is quite different from that obtained from glycerol and the other glycerols only give oily products. All the products of oxidation with bromine of the alkylglycerols reduce Nessler's reagent, Fehling's solution, and ammoniacal silver nitrate.

None of the oxidation reactions with potassium permanganate is specific to glycerol, and the same applies to the oxidation with lead peroxide. W. G.

Modification of Windaus's Method for the Estimation of Cholesterol. Roger Caminade (*Bull. Soc. Chim. biol.*, 1922, **4**, 601—613).—Windaus's method yields irregular results unless the precipitation of the digitonin cholesteride is made under definite conditions. More consistent results may, however, be obtained with much greater rapidity if the precipitate is formed in a solvent consisting of acetone (78 parts), water (18 parts), and alcohol (9 parts). A 5% solution of digitonin in the mixed solvent is added to the hot solution of cholesterol in the same solvent. The precipitate forms immediately, and, after a few minutes, is filtered and washed, first with hot water, then with the mixed solvent, and finally with ether to remove lecithin.

E. S.

Molybdo-manganimetry and its Applications. G. Fontès and L. Thivolle (*Bull. Soc. Chim. biol.*, 1922, **4**, 614—622).—The authors have shown that the volumetric micro-estimation of dextrose (A., 1921, ii, 563) and of lactose (A., 1922, ii, 323) may be conveniently carried out by means of potassium permanganate when used in conjunction with a phosphomolybdic acid reagent. The method appears to be generally applicable to the micro-

estimation of reducing substances, and it is accordingly proposed to class such volumetric methods under the heading "molybdo-manganimetry." The phosphomolybdic acid reagent is reduced by cuprous, ferrous, stannous, and mercurous salts, by sodium hyposulphite, and even by metallic copper, iron, zinc, and magnesium. The blue oxides of molybdenum so produced may be titrated with potassium permanganate, by which they are re-oxidised to molybdic acid, but the details of the method have not yet been worked out for each case. It is shown, however, that the copper deposited on the cathode in Pregl's apparatus for the micro-electrolysis of copper dissolves readily in the phosphomolybdic acid reagent, and that titration of the blue solution so obtained gives results agreeing with those obtained gravimetrically. For purposes of calculation, the reaction is regarded as a direct oxidation of the reducing substance by potassium permanganate; hence, in the estimation of dextrose, the use of a standard may be dispensed with if desired. E. S.

Micro-estimation of Blood-sugar with Ferricyanide. H. C. HAGEDORN and B. NORMAN JENSEN (*Biochem. Z.*, 1923, **135**, 46—58).—A new method which is claimed as superior to Bang's micro-method for the estimation of sugar in 0·1 c.c. of blood has been worked out in detail and depends on the oxidation of the sugar by excess of potassium ferricyanide, the excess being estimated by the iodine liberated in presence of zinc salts from potassium iodide. About eighteen analyses can be carried out in an hour. For details and tables, the original should be consulted. H. K.

Methods of Chemical Investigation on Blood. V. Estimation of Sugar in Blood. ALMA ROSENTHAL (*Biochem. Z.*, 1922, **133**, 469—475).—Details are given of a slightly modified Hagedorn method for the estimation of blood-sugar. After precipitation of the protein by metaphosphoric acid or sodium tungstate, the filtrate is boiled with sodium ferricyanide, and the excess which is not reduced to ferrocyanide is estimated by adding potassium iodide and titrating the iodine liberated with thiosulphate. From the result, the content of the blood in dextrose can be obtained from a table. W. O. K.

The Detection and Identification of Maltose, Galactose, Sucrose, and Inulin by a Mycological Method. ALDO CASTELLANI and F. E. TAYLOR (*J. Trop. Med.*, 1922, **25**, 41—46).—An extension of the previously published method (*Brit. Med. J.*, 1917, Dec. Rep.; *Physiol. Abstr.*, **3**, 263). A table shows the reaction of a number of bacteria and fungi with a great variety of carbohydrates. Fermentation tests with two suitable micro-organisms is sufficient to establish the identity of any of the sugars named (cf. A., 1922, ii, 879). CHEMICAL ABSTRACTS.

Effects of the Method of Desiccation on the Carbohydrates of Plant-tissue. KARL PAUL LINK and W. E. TOTTINGHAM (*J. Amer. Chem. Soc.*, 1923, **45**, 439—447).—In preparing plant-

tissues for carbohydrate estimations, a temperature of 98° should not be used for drying the fresh plant material when the sugar and starch contents are high. With tissue that can be dried rapidly, a temperature of 65° in a current of air at atmospheric pressure can be used safely if the tissue can be reduced to thin sections. When drying in a vacuum, 80° is a better working temperature than 65°, and in the case of coarse tissues improved results are obtained if the material is first heated in an autoclave to inhibit enzymatic and respiratory processes. The results obtained by this method in the case of beet leaves and corn ears were the same as when the alcohol method of preservation (cf. Davis and Daish, A., 1914, ii, 152) was used. Drying at low temperatures with a minimum error can be carried out only in a well-ventilated oven in which a large volume of air circulates continuously over the material. W. G.

Estimation of Incrustating Substances on Flax Fibres by Saccharification of the Cellulose. P. P. BUDNIKOV and P. W. SOLOTAREV (*Z. angew. Chem.*, 1923, **36**, 138—139).—In the purification of flax waste by digesting it under pressure with liquors containing sodium hydroxide and sodium hydrogen sulphite, the cellulose-content of the product was estimated by the method of Ost and Wilkening. In this method, which gave satisfactory results, 1 g. of the purified flax is dissolved in 7—8 c.c. of 72% sulphuric acid and the solution thereby obtained is afterwards diluted until its acid content is 3%, and is then heated for two hours at 120° in an autoclave. The reducing sugars present in the product are then estimated by means of Fehling's solution and the original cellulose-content calculated. (See further, *J.S.C.I.*, 1923, April.) A. J. H.

The Estimation of the Iodine Number of Fats under Unfavourable Conditions. B. M. MARGOSCHES, RICHARD BARU, and LISBETH WOLF (*Z. anal. Chem.*, 1923, **62**, 178—184).—The method of Aschman (*Chem. Ztg.*, 1898, **22**, 59, 71) for the estimation of the iodine number of fats, in which an aqueous solution of iodine monochloride is allowed to react on the fat, gives accurate results, even without the use of a solvent for the fat and without continual shaking, provided that the solutions are left for a sufficient length of time (about twenty-four hours) before the excess of reagent is estimated. This period may be considerably reduced if the fat is dissolved in carbon tetrachloride or other suitable solvent and the mixture frequently agitated. A. R. P.

A Simple Method for the Estimation of Lactic Acid in the Stomach-contents. RICH. EGE (*Biochem. Z.*, 1923, **134**, 476—488).—A method is described for the estimation of lactic acid in the stomach contents, depending on the extraction of the lactic acid by ether, and re-extraction by water before titration. The distribution of lactic acid between ether and water is allowed for. W. O. K.

Cyanogenesis. A Reaction of Citric Acid. A. M. JORISSEN (*Bull. Acad. roy. Belg.*, 1919, 731—737).—The author had previously shown (A., 1914, i, 813) that hydrocyanic acid was formed, under the influence of light, in solutions containing citric acid and traces of iron salts and nitrous acid. Hydrocyanic acid is not formed when citric acid is replaced by formaldehyde, acetaldehyde, formic, lactic, *iso*butyric, or lævulic acids, sucrose, dextrose, gelatin, vanillin, or ethyl acetoacetate (cf. *loc. cit.*). A test is developed using ferric chloride, acetic acid, and potassium nitrite as reagents. It fails in presence of tartaric acid. A more sensitive test is as follows: 100 c.c. of the solution to be tested are treated with 5 g. of manganese dioxide and 5 drops of acetic acid, and the mixture is left for twenty-four hours. After filtration, the liquid is treated with 5 to 10 drops of acetic acid and 5 c.c. of 1% potassium nitrite solution, the mixture left over-night, and then distilled in steam after adding calcium carbonate. The first 130 c.c. of distillate are tested for hydrocyanic acid (ferrous and ferric salt, sodium hydroxide, etc.). Glycerol, lactose, dextrin, and the other substances detailed above do not give rise to hydrocyanic acid under these conditions. E. E. T.

Comparison of the Pentabromoacetone Method, and Salant and Wise's Method for the Estimation of Citric Acid in Urine. W. B. McCLURE and L. W. SAUER (*Amer. J. Physiol.*, 1922, 62, 140—144).—When known amounts of citric acid were added to normal urine the pentabromoacetone method (Amberg and McClure, A., 1918, i, 141) gave much better results than Salant and Wise's method (A., 1917, i, 106) in three cases. In the fourth case, there was close comparison between the results of the two methods. The pentabromoacetone method is preferred by the authors (cf. A., 1922, ii, 791). CHEMICAL ABSTRACTS.

Identification of Benzonaphthol [β-Naphthyl Benzoate], Salol [Phenyl Salicylate], Betol [β-Naphthyl Salicylate], Cresalol [p-Tolyl Salicylate], and Salophen [p-Acetamidophenyl Salicylate] by Microchemical Means. G. DENIGÈS (*Bull. Soc. pharm. Bordeaux*, 1922, 60, 163—169).—β-Naphthyl benzoate: a fraction of 1 mg. of the material is dissolved on a glass slide in a drop of chloroform from a tapered rod of end diameter 2—4 mm.; evaporation leaves crystal groups forming more or less concentric zones. A drop of glacial acetic acid, when placed at the centre of the dry residue and allowed to evaporate, yields arborisations often accompanied by isolated or crossed prisms. If the residue from chloroform or acetic acid is mixed with a drop of concentrated sulphuric acid, and a glass rod which has been dipped into formaldehyde solution inserted, a yellowish-brown colour develops, and on gentle heating the mixture blackens.

Phenyl salicylate, when similarly treated with chloroform, yields an oily droplet, which is not changed by treatment with acetic acid. The residue, by dissolution in a drop of ethyl alcohol, yields by evaporation groups of rhombic plates, similar crystals

being obtained also by seeding the oily droplet with the original material. Treatment as before with sulphuric acid and formaldehyde gives a white cloudiness followed by a red coloration which is intensified by heating.

β-Naphthyl salicylate is deposited from chloroform as an oily droplet; acetic acid then gives isolated rhombic plates mixed with clusters of prisms. With sulphuric acid and formaldehyde, the substance behaves in the same way as β-naphthyl benzoate.

p-Tolyl salicylate yields crystals (m. p. 36°) by seeding the oily droplets obtained from chloroform, acetic acid, ethyl alcohol, acetone, or pyridine. With sulphuric acid and formaldehyde, the substance behaves like phenyl salicylate.

p-Acetamidophenyl salicylate is deposited from acetone as isolated or tangled rhombic plates. When treated with sulphuric acid and formaldehyde, a rose colour develops in the cold; when heated, the colour is intensified at first, and then changes to brown.

CHEMICAL ABSTRACTS.

Demonstration of Salicylic Acid in Serum and Similar Fluids. H. HÉRISSEY (*Bull. Soc. Chim. biol.*, 1922, **4**, 648—651).—The serum is acidified with sulphuric acid, extracted with ether, and the presence of salicylic acid in the latter demonstrated by means of the ferric chloride reaction. E. S.

Estimation of Formaldehyde and Acetaldehyde. E. W. BLAIR and T. S. WHEELER (*Analyst*, 1923, **48**, 110—112).—Mixtures of formaldehyde, hydrogen peroxide, formic acid, and a trace of ozone obtained in investigations on the action of oxygen and ozone on hydrocarbons were analysed as follows. Formic acid was estimated in an aliquot part by titrating with *N*/100-alkali, methyl-red or phenolphthalein being used as indicator. Ozone was estimated in the neutralised solution by adding a 5% neutral solution of potassium iodide, acidifying with 5% hydrochloric acid free from chlorine, and immediately titrating the iodine liberated with *N*/100-thiosulphate solution. The hydrogen peroxide was estimated by Kingzett's method (T., 1880, **37**, 802). To estimate the formaldehyde, the ozone and hydrogen peroxide were destroyed by adding potassium iodide and sulphuric acid. The iodine set free was not titrated, but the diluted solution was just neutralised, with thorough cooling, with sodium hydroxide solution. Twenty-five c.c. of *N*/10-iodine solution were then added and the formaldehyde estimated by Romijn's iodometric method (A., 1897, ii, 166), allowance being made for the iodine set free in previous reactions. If acetaldehyde was also present, Ripper's method (A., 1901, ii, 205) was used to obtain an iodine figure for both aldehydes, and the cyanide figure (Sutton, "Volumetric Analysis," 10th ed., p. 391) for formaldehyde applied to it to estimate the acetaldehyde present. H. C. R.

A Micro-method for the Estimation of Acetone and of β-Hydroxybutyric Acid in Urine and Blood. ALFRED LUBLIN (*Biochem. Z.*, 1922, **133**, 626—641).—A micro-method is described

for the estimation of acetone and of β-hydroxybutyric acid in 0·2 c.c. of blood, or in 0·5 c.c. of urine, the estimation requiring thirty minutes in the first case and twenty minutes in the second. The acetone is distilled into an alkaline iodine solution, and the iodine left is titrated with thiosulphate. W. O. K.

Reaction of Phenolphthalein. G. DE BENAVENT (*Anal. Fis. Quim.*, 1922, 20, 473—474).—An alkaline urine containing phenolphthalein, previously administered, and eliminated by the kidneys, was found to lose its red coloration on heating, whilst on cooling the red coloration reappeared. The reaction is shown to be due to the presence of uric acid. A number of other organic acids were examined for this reaction which was, however, only given by salicylic acid and benzoic acid in addition to uric acid.
G. W. R.

Estimation of Amino-acids and Ammonia, using an Apparatus to Control the Distillation. GIOVANNI REVOLTELLA (*Biochem. Z.*, 1922, 134, 349—353).—The formal titration of amino-acids in pigmented urine is facilitated by using a colour match of the same urine instead of water as used by Sörensen. An apparatus is also described which is designed to show when the evolution of ammonia is finished in a distillation. H. K.

Estimation of Codeine. HAROLD EDWARD ANNETT and RAM RICHHPAL SANGHI (*Analyst*, 1923, 48, 16—18).—Eight g. of opium are triturated with 2 g. of freshly slaked lime and 80 c.c. of water for thirty minutes, 50 c.c. of the filtrate are extracted three times with 50 c.c. portions of toluene, the filtered extract is concentrated to 25 c.c., dry hydrogen chloride is passed through, and the precipitated codeine hydrochloride and colouring matter are dissolved in water and evaporated to dryness, thereby rendering the colouring matter insoluble. The residue is treated with hot water, the volume adjusted to 50 c.c., and the whole process is repeated from the beginning with 40 c.c. of the filtrate from the lime treatment (=4 g. of opium). In the final evaporation no further colour should develop, and the addition of a little alcohol when nearly all the water has evaporated causes the separation of codeine hydrochloride in small, colourless rosettes. The residue is dried to constant weight in a steam oven and taken as

$$C_{18}H_{21}O_3N,HCl,1\tfrac{1}{2}H_2O.$$

The method was tested with pure codeine, and on opium with and without added amounts of codeine, and 95—96% of the codeine present was regularly recovered. G. F. M.

Estimation of Narcotine and Papaverine in Opium. H. E. ANNETT and M. N. BOSE (*Analyst*, 1923, 48, 53—58).—Opium (1·5 g.) is triturated to a smooth paste with 30 c.c. of 0·5% sulphuric acid and after thirty minutes 20 c.c. of the filtrate are boiled with 16 g. of sodium acetate until complete solution of the salt has been effected. After keeping over-night the liquid is

filtered, the precipitate completely transferred to the filter-paper, washed, and dried. It is then extracted with 20—25 c.c. of hot toluene, the toluene extract is shaken with 20 c.c. of 10% sodium hydroxide to remove resins and colouring matters, and the washed toluene solution is evaporated almost to dryness with the addition of 2—3 c.c. of alcohol to facilitate crystallisation of the narcotine and papaverine, which after drying at 100° are weighed as such. The narcotine can then be estimated polarimetrically, papaverine being optically inactive. The rotation is measured in toluene solution as in acid solution papaverine considerably depresses the optical activity of narcotine. The process was tested on opium with and without the addition of known amounts of the two alkaloids, and satisfactory results were obtained without the use of any correction factor. G. F. M.

A Rapid Process for the Exact Estimation of Small Quantities of Uric Acid in Urine and in Blood-serum. HEINRICH CHANTRAINE (*Biochem. Z.*, 1922, **133**, 605—612).—Uric acid in urine is separated as in Hopkin's method by the addition of ammonia and ammonium chloride, after precipitating it as the copper salt, and liberating it from that with hydrogen sulphide. Excess of potassium permanganate solution is added to the uric acid, and the excess is estimated iodometrically. A similar method may be used for estimating uric acid in blood-serum. W. O. K.

Behaviour of Uric Acid in Protein Solutions. LUDWIG PINCUSSEN (*Biochem. Z.*, 1923, **134**, 447—458).—Uric acid in serum is only partly free, and results obtained on estimation are increased if the protein is first hydrolysed by a ferment or an acid, as only the free uric acid is determined by these methods. Other proteins and also fats, lipoids, etc., combine with uric acid.

W. O. K.

The Iodometric Estimation of Antipyrine. I. M. KOLTHOFF (*Pharm. Weekblad*, 1923, **60**, 194—199).—Very good results are obtained by the method of Bougault (A., 1917, ii, 344), namely, addition of excess of $N/10$-iodine solution in presence of sodium hydrogen carbonate, acidification after one hour, and titration back with thiosulphate after addition of chloroform. The reaction is $C_{11}H_{12}ON_2 + I_2 = C_{11}H_{11}ON_2I + HI$. Sodium acetate may be used in place of the hydrogen carbonate, and alcohol in place of chloroform. The results are not affected by the presence of sodium salicylate, caffeine, acetanilide, phenacetin, or aspirin. S. I. L.

Measurement of the Colour of Brown Solutions, with Special Reference to Tannin Extracts. HENRY R. PROCTER (*J. Soc. Chem. Ind.*, 1923, **42**, 73—79T).—The colours of brown solutions, more especially of tannin extracts, are determined by observing by means of a spectro-colorimeter the depth of solution required to reduce the light transmitted by the solution to a definite fraction of its initial value, *e.g.*, one-half. Observations are made

with red, yellow, green, and blue light of definite wave-lengths. Alternatively, colour screens of copper-ruby and copper-green glass and a screen containing a solution of copper sulphate made alkaline with ammonia may be employed to afford light of sufficiently definite composition. In this case the rotating neutral tint sector of the spectro-colorimeter is replaced by a 20% solution of iron alum, and the colour of the tannin extract compared with the colour of this solution. J. S. G. T.

The Estimation of Albumin by the so-called Nephelometric Processes. HENRI BÉNARD and ALBERT LABORDE (*Compt. rend.*, 1923, **176**, 98—101).—A comparison of the results obtained by a diffusimeter of the type of Baudouin and Benard (*Compt. rend. Soc. Biol.*, 1920, May) and by an opacimeter of the type of Cheneveau and Audubert (A., 1920, ii, 327) in the estimation of albumin in blood-serum, using trichloroacetic acid as a precipitant. The final dilutions were of the order of 2—40 per 100,000. In the diffusion method a control curve is necessary at the higher concentrations. The opacimeter can be used, if arranged vertically, in cases where the precipitate settles rapidly, as the thin sediment gives the same reading as the initial suspension. The diffusimeter is, however, more sensitive for very dilute emulsions. W. G.

Estimation of Trypsin and Pepsin. JOHN H. NORTHROP and RAYMOND G. HUSSEY (*J. Gen. Physiol.*, 1923, **5**, 353—358).—Estimation of trypsin (or pepsin) may be effected by measuring the change in a definite time and at a given P_H and temperature in the viscosity of purified gelatin to which a given amount of the trypsin solution has been added. It is found that the time taken to cause a given percentage change in the viscosity is approximately inversely proportional to the amount of trypsin added. W. O. K.

Arginase. VI. Modification of the Volumetric Method for Detecting Arginase. ANTONINO CLEMENTI (*Atti R. Accad. Lincei*, 1922, [v], **31**, ii, 454—459).—If the acid liquid obtained by the acid hydrolysis of edestin, or the phosphotungstic precipitate of hexone bases obtained therefrom, is treated in vitro in presence of toluene with the pulped liver of a mammifer (monkey, man, rat) which contains arginase, a considerable increase is effected in the proportion of nitrogen titratable with formaldehyde. No such increase occurs, however, if the above liver is first boiled or if hen's liver, which is devoid of arginase, is used. The conclusion is drawn that the increase in nitrogen titratable with formaldehyde corresponds with the ornithine formed by scission of the arginine by the arginase, and that such increase furnishes an indication of the presence of arginase in an organ or in an organic liquid. T. H. P.

A New Reaction of the Blood. GIUSEPPE BECCADELLI (*Biochem. Z.*, 1922, **134**, 180—182).—If to 0·5 c.c. of serum or blood

there be added equal volumes of formaldehyde (40%), silver nitrate (0·75%), and ammonia (0·9%), after a few minutes the solution acquires a colour depending on the origin of the serum. Normal human serum gives an amber colour, that of various animals a shade of yellow, whilst that of syphilitics is decolorised.

H. K.

A Sensitive Reaction for Neo-salvarsan. K. SCHERINGA (*Pharm. Weekblad*, 1923, 60, 248).—One drop of a solution of one part in a thousand gives a violet coloration to a concentrated solution of ammonium persulphate. Colorations are given more or less quickly with other organic substances which form coloured oxidation products, salvarsan also giving a violet colour, but the reaction with neo-salvarsan is much more sensitive. S. I. L.

Estimation of the Grignard Reagent. H. GILMAN, P. D. WILKINSON, W. P. FISHEL, and C. H. MEYERS (*J. Amer. Chem. Soc.*, 1923, 45, 150—158).—Five methods for the estimation of Grignard's reagent have been studied, namely, titration with iodine (cf. Jolibois, A., 1912, i, 675), gravimetric analysis by the preparation of some insoluble compound, indirect analysis, gas analysis, and titration with acid.

Of these methods, the first was rejected as giving results which varied considerably with slight alterations in the conditions, the second was rejected as being unsuitable and giving low results. Of the three remaining methods, the last two, namely, the method of gas analysis and that of titration with acid, gave satisfactory results. They are based on the smooth decomposition of the Grignard compound with water, the gas evolved being measured in one method, and the basic magnesium halide titrated with standard acid in the other method. For the gas analysis method, an apparatus somewhat of the type of Van Slyke's apparatus for the estimation of amino-acids is used. For the titration method, the known volume of solution containing the Grignard reagent is warmed with a known excess of standard acid until all the basic magnesium halide is dissolved, and then the excess of standard acid is titrated back with standard sodium hydroxide, using methyl-orange as indicator. W. G.

General and Physical Chemistry.

Refractivity of Organic Fluorine Compounds. FRÉD. SWARTS (*J. Chim. Phys.*, 1923, 20, 30—76).—The refractivity of a large number of organic fluorine derivatives is recorded. In the case of substituted paraffins, the introduction of fluorine decreases the molecular refraction by an amount which decreases the longer the carbon chain, and increases with the refrangibility of the light. Thus the molecular refractivity calculated by the Lorentz-Lorenz formula $[R_L]_\lambda$ has the following values: C_5H_{12}, $_\alpha$, 25·131; $_\beta$, 25·522; $_\gamma$, 25·748; $C_5H_{11}F$, $_\alpha$, 24·99; $_\beta$, 25·350, $_\gamma$, 25·569; C_7H_{16}, $_\alpha$, 34·452; $C_7H_{15}F$, $_\alpha$, 34·364; C_8H_{18}, $_\alpha$, 39·073; $_\alpha$, $C_8H_{17}F$, 39·032. Using the values of hydrogen found by Brühl, Landolt, and Falk, the atomic refractivity of fluorine is $[R_L]_\alpha$, 1·014, $[R_L]_\beta$, 1·005, and $[R_L]_\gamma$, 1·003. With methyl *cyclo*hexane, the accumulation of fluorine does not produce any exaltation in the refractive value of the substitution $H \rightarrow F$. In the case of alcohols and esters, it is shown that the substitution of one fluorine atom produces a depression in the molecular refractivity of the same order as that observed with the paraffins, whereas the introduction of a second fluorine atom gives no depression with difluoroethyl alcohol, but a strong exaltation in difluoroethyl acetate. With acetic acid, the introduction of fluorine increases the molecular refractivity, which further increases with each fluorine atom introduced. Thus with H_α light, the increase for the first fluorine introduced is 0·13, for the second 0·31, and for the third 0·41. Measurements are also recorded for fluorine-substituted ketones, aldehydes, and amines. In the case of ethylene compounds, it is shown that the two stereoisomerides of bromofluoroethylene have practically the same molecular refractivity, although their densities are somewhat different. Tables of the dispersion of a large number of derivatives are given. In the case of aromatic compounds, it is shown that fluorine is unique in the fact that it alone gives derivatives which have a smaller refractivity than the corresponding open-chain compounds for all wave-lengths. The anomalies observed in the refractivity of fluorine compounds are considered in connexion with the structure of the fluorine atom. The following hitherto unpublished physical data for fluorine compounds are recorded: *Ethyl* o-*fluorobenzoate*, b. p. 216—216·5°/756 mm., m. p. −21·3°; m-*fluorobenzonitrile*, b. p. 182·6°/753 mm., m. p. −16·05°; *ethyl* m-*fluorobenzoate*, b. p. 208·8—208·84°/757·2 mm., m. p. −33·5°; *ααα-3-tetrafluorotoluene*, b. p. 101·2°; trifluoromethyl*cyclo*hexane, b. p. 103·20°, m. p. −103·4°; difluoromethyl*cyclo*hexane, b. p. 129·2°; ethyl trifluoroacetate, b. p. 5°. J. F. S.

The Stark Effect on the Secondary Spectrum of Hydrogen. MASAZÔ KIUTI (*Japan. J. Physics*, 1922, 1, 29—39).—An investigation into the behaviour of the lines in the secondary

spectrum of hydrogen of long wave-length, and including the Fulcher bands, under the influence of a powerful electrical field. From the blue to the red, more than one hundred lines are affected, but those lines on the long wave-length side of 5300 Å. do not usually show the Stark effect. The lines are normally displaced towards the red, or else separated in an asymmetrical manner. Groups of lines in the neighbourhood of 5400 Å. and 5930—5982 Å. are very largely affected. The amount of displacement increases either in proportion to, or more rapidly than, the field intensity. No simple rule can be found for the Stark effect on the Fulcher bands, except that the effect on the first and third members of both of the two bands is large and small alternately in the homologous succession of lines. This alternation may give some suggestion as to the structure of the centre of emission of the secondary spectrum. W. E. G.

Line Spectrum of Chlorine in the Ultra-violet (Region λ 3354—2070 Å.). W. JEVONS (*Proc. Roy. Soc.*, 1923, [*A*], 103, 193—204).—Using a 10-foot concave grating and a quartz spectrograph, the author has investigated the ultra-violet spectrum of chlorine in the region λ 3354—2070 Å. A condensed discharge from a 12-inch induction coil with one, two, or three Leyden jars was employed, and a spark-gap of about 1 cm. was placed in series with the discharge tube. The spectrum was observed end-on to the capillary through a quartz window. Precautions were taken to eliminate lines due to impurities, and it is considered improbable that any oxygen lines remained unidentified, except possibly below λ 2228 Å. About two hundred lines due to chlorine were recorded, and the effect of capacity on the estimated intensities of more than one hundred of these was studied. The following lines, attributed by Exner and Haschek to chlorine were not observed: λ 3291·1, 3261·6, 3248·5, 3221·1, 2960·5, 2936·7, 2928·8 Å. The line λ 3129·5 Å., similarly attributed by Exner and Haschek, was observed but was probably due to oxygen. No triplets having constant differences of wave-number intervals 40·44, 67·10, and 107·88, respectively, as suggested by Paulson, were observed, but six pairs with a constant difference $\Delta\nu=40\cdot4\pm1\cdot0$, four pairs having $\Delta\nu=67\cdot1\pm1\cdot0$, and five pairs having $\Delta\nu=107\cdot5\pm1\cdot0$ were found. J. S. G. T.

Band Spectra of Mercury. HANTARO NAGOAKA (*Japan. J. Physics*, 1922, 1, 1—6).—A *résumé* of preliminary work on the band spectra of mercury. The discordances between the results of different physicists on the band spectra of mercury may be attributed to the methods of construction of the lamps used. In this work, a lamp has been devised which gives nearly all the spectra previously recorded. Approximate measurements of the positions of the heads of the bands have been made. In some of the bands which could be easily measured, Deslandres's formula gives the positions of the lines accurately. Experiments were made to determine the structure of the lines in the bands, but no evidence was obtained of the presence of companions in the form of satellites.

Since this work was not conclusive, however, further experiments are being carried out with the aid of a high resolving spectrometer.
W. E. G.

Tesla-luminescence Spectra. III. The Effect of Varying Temperature and Pressure on the Benzene Spectrum. WILLIAM HAMILTON MCVICKER and JOSEPH KENNETH MARSH (T., 1923, **123**, 817—820).

The Fluorescence Spectrum of Benzene Vapour. WILLIAM HAMILTON MCVICKER and JOSEPH KENNETH MARSH (T., 1923, **123**, 820—822).

The Infra-red Absorption of Hydrogen Chloride in the Region 3·5 μ, and at 200° *K*. B. J. SPENCE and C. HOLLEY (*J. Opt. Soc. Amer.*, 1923, 7, 169—173).—The infra-red absorption bands of hydrogen chloride have been measured at 291° and 200° *K*. They consist of two groups of bands of which the maxima of the envelopes occur at 3·397 μ and 3·538 μ at 291° *K*, and at 3·419 μ and 3·514 μ at 200° *K*. One-half of the frequency difference between the maxima of the envelope of the absorption bands corresponds with the most probable value of the frequency of rotation of the molecule. According to Kemble (*Physical Rev.*, 1916, **8**, 689), this frequency $f_r = 1/4\pi\sqrt{RT/NJ}$, and thus should depend on the temperature. This equation is in fairly good agreement at 291° *K*, but at 200° *K* there is a divergence indicating that it may require some modification at low temperatures. The position of the fine bands, in agreement with the theory of Bjerrum, is independent of the temperature. The results are also in accord with the theory of Reiche (*Ann. Physik*, 1919, **58**, 657), according to which, at 291° *K*, the position of maximum absorption should occur at the third fine band, and at 200° *K* at the second band on each side of the centre. W. E. G.

The Limits of Absorption *K* of certain Elements. J. CABRERA (*Compt. rend.*, 1923, **176**, 740—741).—The limits of absorption *K* of the elements of the rare earths were determined using de Broglie's method with a rotating crystal spectrograph and a lead screen with a window filled with the substance under examination. A Coolidge tube with a tungsten anticathode, or, in the case of thulium, where the limit of absorption *K* is very near the $K_{\alpha 1}$ line of tungsten, a gas tube with a platinum anticathode. The limit of absorption for tantalum was also measured. The results are given in tabular form, from which it is seen that the values of $\sqrt{\nu/R}$ depart more and more from a simple linear relation as the series of atomic numbers is ascended. G. F. M.

The Law of the Distribution of the Bands in the Ultraviolet Absorption Spectrum of the Vapour of Toluene. VICTOR HENRI and E. WALTER (*Compt. rend.*, 1923, **176**, 746—748).—The absorption spectrum of toluene vapour is composed of more than two hundred narrow bands distributed between λ 2731 and

λ 2325. The law of the distribution of these bands is expressed by the formula

$$1/\lambda = A + n \, . \, a + p \, . \, b - qc - h/(8\pi^2 \, . \, 3 \, . \, 10^{10} \, . \, \mathfrak{J})(1 \pm 2m)$$

where A, corresponding with the electronic impulses, is 37493·2, a, b, and c with the vibrations of the atoms are 932·5, 263·6, and 180, respectively. $\mathfrak{J}$ is the moment of inertia of the rotation of the molecule, m, n, p, and q are whole numbers, and $h/8\pi^2 \, . \, 3 \, . \, 10^{10} \, . \, \mathfrak{J} =$ 1·3. The intensity of the bands diminishes as the values of n, p, and q increase. The moment of inertia of the toluene molecule $\mathfrak{J} = 21 \cdot 10^{-40}$. G. F. M.

Ultra-violet Absorption Spectra of Benzoic Acid and the Three Hydroxybenzoic Acids. ARMAND CASTILLE and F. W. KLINGSTEDT (*Compt. rend.*, 1923, **176**, 749—750).—The introduction of a carboxyl group into the benzene nucleus causes a displacement of the absorption spectrum by about 230 Å. towards the red, a quadruple increase in the coefficient of adsorption, and a widening of the absorption bands. The introduction of a hydroxyl group into the benzoic acid molecule in either the ortho- or meta-position is accompanied by a great increase in the absorption, a further widening of the narrow bands, and a considerable displacement of the spectrum towards the red. The two derivatives have almost the same spectrum. The para-derivative, on the other hand, is characterised by an entirely different spectrum, which shows five narrow bands between λ 2828 and 2671, then a wide and intense band at λ 2519, and an inflexion towards λ 2100, showing the existence of a band in this neighbourhood which is fused with a wide band in the extreme ultra-violet. These results are comparable with those obtained with other ortho-, meta-, and para-derivatives of benzene. G. F. M.

The Ultra-violet Absorption Spectra of Veratrole and Vanillin. PIERRE STEINER (*Compt. rend.*, 1923, **176**, 744—746).—The absorption curve of veratrole is very similar to that of pyrocatechol, the introduction of two methyl groups into the molecule having but little influence on the absorption. There is a group of three narrow bands in the middle ultra-violet, and a fourth band broad and very pronounced in the extreme ultra-violet. The absorption curve of vanillin can be compared with that of pyrocatechol and veratrole, on the one hand, and of benzaldehyde, on the other. The same three narrow bands are found as in veratrole, but displaced somewhat towards the red, and three times as intense. There is, in addition, a new broad band in the middle ultra-violet which is attributable to the aldehyde group, and the broad band of veratrole in the extreme ultra-violet appears again in vanillin, displaced slightly towards the right, and twice as intense.

G. F. M.

Studies in Organic Compounds containing Sulphur. I. The Effect on General Absorption due to the Valency and Mode of Linking of the Sulphur Atom. DAVID TEMPLETON GIBSON, HUGH GRAHAM, and JAMES REID (T., 1923, **123**, 874—881).

The Absorption of Light by Hæmatoporphyrin. I. KIKO GOTO (*Biochem. Z.*, 1923, **135**, 328—343).—Four different preparations of pure hæmatoporphyrin have been submitted to spectrophotometric measurements in dilute alcoholic solution with or without the addition of ammonia, acetic acid, or hydrochloric acid. In neutral, ammoniacal, or acetic acid solution, the curves obtained by plotting the specific extinction coefficient against the wave-lengths show very good agreement in detail over the four absorption bands. When, however, the solutions are left exposed to the light of a metallic filament lamp for periods up to twelve hours, the bands change, the first and fourth disappearing, and the second and third becoming merged more or less into one. In alcoholic solution to which concentrated hydrochloric acid had been added, there is only one absorption band, and it is unaffected by light. H. K.

The Absorption of Light by Hæmatoporphyrin. II. PAUL HÁRI (*Biochem. Z.*, 1923, **135**, 344—352).—The author has examined, spectrophotometrically, the colouring matter in the urine of a patient in an undetermined pathological condition, and although the colouring matter was apparently closely allied to hæmatoporphyrin, it was not identical, the positions of the bands in alcoholic-ammoniacal solution and alcoholic-hydrochloric acid solution being different from those of hæmatoporphyrin (see preceding abstract). H. K.

The Absorption of Light by several Components. N. P. PESKOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1924—1952).—Mixtures of coloured substances are examined spectrophotometrically with a view to ascertaining what mutual influences their components have on each other. Only crystalloids follow Beer's law, separately, or in mixtures. The use of dyes, which are mainly colloidal substances, together with crystalloids is useless for the purpose of testing Beer's law, and the absorption constants of such mixtures cannot be calculated by this law. The importance of this observation in connexion with the preparation of quantitative light filters for the determination of wave-lengths is pointed out. Mixtures of colloids only in exceptional cases follow Beer's law, but usually vary from it owing to inter-adsorption of the components, and light filters made from mixtures of such substances must therefore in each case be separately calibrated. Thus in the case of a mixture of colloidal iron and malachite-green, the latter substance distributes itself between the water and the colloidal hydrated ferric hydroxide in a constant ratio, depending on the concentrations of the two components. The value of spectrophotometric analysis for the investigation of the detailed processes of a reaction and the identification of intermediate products is emphasised. R. T.

The Fluorescence and Coloration of Glass produced by β-Rays. J. R. CLARKE (*Phil. Mag.*, 1923, [vi], **45**, 735—736; cf. A., 1921, ii, 569).—Glass tubing, after treatment with radium

emanation until the colour change is complete, is heated at different temperatures and the duration of fluorescence measured. The time of fluorescence ranges from thirteen minutes at 110° to thirty seconds at 350°. At the annealing temperatures, the decolorisation will be practically instantaneous. Since at these temperatures complex molecular changes take place, it is probable that the fluorescence and decolorisation of the glass are associated with changes in the state of molecular aggregation. The normal colour of the radiated glass is brown, but when manganese is present it is purple. W. E. G.

Rotatory Power of Organic Compounds. H. RUPE (*J. Chim. Phys.*, 1923, **20**, 87—104).—A lecture on rotatory power delivered at Fribourg, Switzerland, April 30, 1922. J. F. S.

Inhibition of the Photochemical Decomposition of Hydrogen Peroxide Solutions. I. WILLIAM THEODORE ANDERSON, jun., and HUGH STOTT TAYLOR (*J. Amer. Chem. Soc.*, 1923, **45**, 650—662).—The rate of decomposition of hydrogen peroxide by ultraviolet light of wave-length λλ 2000, 2650, 2930, and 3050, respectively, has been determined, and the inhibitory effect of some twenty-five organic substances of widely differing character examined at 25°. All such substances inhibit the decomposition, due to the absorbing of the light by the organic compounds, and this has been found to be true in the case of benzene, several esters, acids, amines, ketones, and alkaloids. The retarding action of amines and alcohols requires an explanation based on causes other than absorption. It is shown that the inhibitors act more efficiently when placed in the peroxide solution than when used as a screening solution of similar thickness and concentration. The reason of the more efficient functioning of the inhibitor in the solution is probably that one quantum of energy is capable of activating more than one molecule. Thus if the stabiliser is acting as a screening solution, the peroxide being free from inhibitors, a quantum of light energy may slip through and enter the peroxide solution and by successive activation decompose a number of molecules. On the other hand, if the stabiliser is in the peroxide solution and one quantum of light energy should succeed in activating a peroxide molecule, this molecule will decompose, liberating the energy quantum, which in its turn may activate another peroxide molecule or, coming within the sphere of influence of a molecule of inhibitor, may be converted into the less active ultra-red energy. J. F. S.

Application of the Photochemical Law of Equivalence to Dilute Solutions. HEINZ GRÜSS (*Z. Elektrochem.*, 1923, **29**, 144—150).—In continuation of the work of Noddack (A., 1921, ii, 568), the author finds that the photochemical reaction $2CCl_3Br+Cl_2+h\nu=2CCl_4+Br_2$, in a medium consisting either of carbon tetrachloride or silicon tetrachloride, proceeds in a manner independent of the concentration of the trichlorobromomethane, at least down to a molecular concentration of 1/80 CCl_3Br in the former medium and 1/60 CCl_3Br in the latter. The results obtained

indicate that pure carbon tetrachloride is a non-acceptor of chlorine under the influence of light. Results contrary to this conclusion, reached by Noddack (*loc. cit.*) and by Plotnikov (A., 1920, ii, 211; 1922, ii, 248) are attributed to the presence of impurities in the carbon tetrachloride employed by them. The reaction $2CCl_3Br+O_2=2COCl_2+Br_2+Cl_2$ can be influenced photochemically, and the velocity of reaction is independent of the concentration of CCl_3Br and O_2 in carbon tetrachloride. Einstein's photochemical law applies to the reaction, and one molecule of bromine is produced per quantum of illumination. The results obtained by Noddack and in the present work indicate that reaction occurs between trichlorobromomethane and illuminated chlorine molecules characterised by a large Bohr quantum number, without previous dissociation into atoms. The lower limit for the period of existence of the molecules in such quantised condition, found from the reaction $2CCl_3Br+O_2+h\nu=2COCl_2+Br_2+Cl_2$ is 10^{-7} sec., compared with 2×10^{-9} sec. in the case of the reaction studied by Noddack. J. S. G. T.

Photolysis of Tartaric Acid and Hydroxy-acids. VOLMAR (*Compt. rend.*, 1923, **176**, 742—744).—Under the influence of ultra-violet light, and to a much lesser degree in sunlight, hydroxy-acids and their salts undergo photolysis. Tartaric acid in 1% solution after three hours' exposure gave 3·5 c.c. of gas having the composition CO_2 66%, CO 10%, H_2 21%, hydrocarbon 3%. The solution contained aldehydes and small quantities of a reducing substance of the nature of a sugar. In presence of alkalis, the carbon monoxide may disappear entirely, owing to condensation with a portion of the hydrogen with formation of the above-mentioned aldehydic substances. The homologues of tartaric acid behaved in a similar way. The decomposition is accelerated by the presence of catalysts such as uranyl acetate. G. F. M.

Spectrophotoelectrical Sensitivity of some Halide Salts of Thallium, Lead, and Silver. W. W. COBLENTZ and J. F. ECKFORD (*U.S. Bureau of Standards, Sci. Papers*, 1922, **18**, 489—498; cf. this vol., ii, 51).—A definite relationship exists between crystal structure, chemical constitution, and atomic weight and spectrophotoelectrical sensitivity. The photoelectrical reaction of the halide salts of thallium, lead, and silver is confined to a narrow region at the violet end of the spectrum, being the narrowest and most sharply-defined reaction spectra of all substances yet investigated, including the photoelectrical gas ionic reaction spectra of the alkali metals. With increase in the atomic weight of the acid element, the maximum of photoelectrical reaction is shifted towards the long wave-lengths. The maximum of sensitivity of thallium chloride lies at 0·368 μ, of the bromide at 0·413 μ, and of the iodide at 0·455 μ. The position of the maximum for the latter is unaffected by lowering the temperature. The reaction curves are unsymmetrical, terminating abruptly on the long wave-length side, and giving a high photoelectrical reaction on the short wave-length side of the maximum. Lead iodide is the only lead halide which is

sensitive, and this gives a complex curve, showing an ill-defined maximum in the region of 0·45 μ and a sharply defined maximum at 0·52 μ. Silver halides are sensitive only when in a fused state, the chloride giving a maximum at 0·38 μ, the bromide at 0·46 μ, and the iodide at 0·47 μ and 0·50 μ, respectively. Silver and potassium nitrates are not sensitive. W. E. G.

Various Photoelectrical Investigations. W. W. COBLENTZ (*U.S. Bureau of Standards, Sci. Papers*, 1922, **18**, 585—607).—Artificial preparations of molybdenum disulphide are not nearly so photoelectrically sensitive as the native mineral, especially that containing a relatively high iron content. The sensitivity is destroyed by heating above 700°, whereas that of stibnite is unaffected under similar treatment.

Curves showing the photoelectrical sensitivity to light of different wave-lengths for cuprous oxide, a native lead-antimony sulphide, Pb_3SbS_3, and iodine are given. Sulphides of tin, tungsten, and uranium, nitrates of silver and potassium, bismuth telluride, and molybdenum selenide are not photoelectrically sensitive. [Cf. *J.S.C.I.*, 1923, May.] A. R. P.

Some Properties of Resonance Radiation and Excited Atoms. K. T. COMPTON (*Phil. Mag.*, 1923, [vi], **45**, 750—760; cf. Horton and Davies, this vol., ii, 4).—Atoms and molecules in states of partial or complete ionisation, produced by suitable excitation, give to a gas properties quite different from those of the normal unexcited gas. Such properties include new lines in the absorption and resonance spectra, the production of band spectra as the result of molecular combination between the excited atoms, and increased ease of ionisation. The excited state in helium gas was shown by Kannenstine to persist for 0·0024 sec. after the exciting voltage was removed. This permanence of excitation was ascribed to the occurrence of metastable helium atoms possessing a long life period. An alternative interpretation of this result is put forward in this paper. An electron the velocity of which exceeds that gained by falling through the resonance potential, V, collides with an atom, and displaces an electron from the normal to an outer orbit forming an excited atom. At the end of the average life of this atom, T, the electron falls back to the normal position, emitting its resonance radiation. Any other normal helium atom is capable of absorbing this radiation and emitting it after an interval, T. The radiation is thus passed from atom to atom until it finally escapes, or is degraded to a non-resonance radiation. The time, 0·0024 sec., in Kannenstine's work will thus represent the time required for the resonance radiation to escape from the gas. The passage of resonance radiation through a gas may be treated as a problem in diffusion, and it is shown that the number and persistence of excited atoms depend jointly on the time of activation, T, and on the square of the scattering coefficient, α^2, of the resonance radiation. From this method of treatment, it appears that the average life of the excited helium atom is not noticeably larger than that predicted by theory, or

very different from that of other substances. In the presence of impurities, the resonance radiation may be altered in character by transformation into other wave-lengths to which the gas is more transparent. Thus the diffuse nature of the line corresponding with the helium atom excited by 20·4 volts may be ascribed to the production of unstable helium compounds between this atom and the impurities. W. E. G.

Critical Electron Energies in Helium, and the Extreme Ultra-violet Spectrum. ANN CATHARINE DAVIES (*Phil. Mag.*, 1923, [vi], **45**, 786—798; cf. A., 1921, ii, 672).—The value of the ionisation voltage for electrons in helium deduced from the lines in the extreme ultra-violet observed by Lyman (cf. A., 1922, ii, 674) is greater than the experimental values of Horton and Davies, and those of Franck and Knipping by 0·7 volt. In the present paper, the errors likely to arise in the experimental values of the former workers are discussed. The discovery of two critical radiation voltages of helium separated by only 0·8 volt introduces the possibility that an error of interpretation of the observed effects has been made. The first of these voltages, at 19·7 volts (corrected), gives a much smaller radiation current than the second at 20·5 volts, and it is possible that the positive current due to the photoelectric effect of the former was so small that it was masked by the negative current from electrons escaping collision; hence the first critical stage was missed in the earlier investigation. Thus the second critical stage may have been taken for the first, in which case the true value for the first critical radiation voltage is $0·8\pm0·1$ volt lower than the value given originally for this constant. Since the values given in subsequent papers were measured relatively to the first, a correction of the same amount must be applied to them also. The selection principle of Bohr does not appear to hold for transitions of electrons to the normal state. Evidence is brought forward to show that the transitions $N-1\sigma$ or $N-1S$ must be possible. An explanation is given of the absence of the line $N-1S$ from the Lyman spectra. The ability of current-voltage observations to reveal the existence of ultra-violet series spectra is discussed, and it is concluded that whereas the method may be expected to indicate the first lines of a series involving the return of an electron to the normal state, it would probably not reveal the higher members of those series. W. E. G.

Excitation and Ionisation Potentials of Neon and Argon. G. HERTZ (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **25**, 442).—In a recent paper (A., 1922, ii, 733) the author described the measurement of the excitation and ionisation potentials of argon and neon and based his calculations on the value 20·45 volts as the first ionisation potential of helium. Franck (A., 1922, ii, 811) has shown that this value is too high and that the figure 19·75 volts is much nearer the correct value. Using this value, the author has recalculated his results. The following values are recorded: Neon, excitation potentials 16·65 and 18·45 volts, ionisation potential 21·5 volts; argon, excitation potentials, 11·55, 13·0,

and 14·0 volts, ionisation potential 15·3 volts. The conclusions relating to the optical spectrum are not affected by this correction, since only the potential differences are used for them. Only the term 0·5 *s*, which corresponds with the normal state of the atom, must be diminished, and becomes 174000±1000 for neon and 124000±1000 for argon. J. F. S.

Critical Velocity of Electrons in Krypton and Excitation of the Spectrum of the Gas. Georges Déjardin (*Compt. rend.*, 1923, **176**, 894—897).—The critical velocity of electrons in krypton and the development of its spectrum was studied by means of the apparatus and method previously employed for argon and helium (this vol., ii, 47, 112). An incandescent filament of tungsten was used as the source of the electrons. The ionisation potential of krypton was found to be 12·7±0·2 volts, and the potential of double ionisation (simultaneous removal of two peripheral electrons) 28·25±0·5 volts. A redetermination of the corresponding values for argon gave 15·2±0·2 volts and 34·0±0·5 volts, respectively. When the pressure is of the order of 1 mm., the ionisation of argon can be observed to commence at 11·5 volts and of krypton at 9·8 volts. These potentials are probably resonance potentials. The ratios of the simple and double ionisation potentials of argon and krypton are equal within the limits of experimental error, which points to the identity of the structure of the peripheral layers of the atoms of the two gases. Krypton has, like argon, two entirely distinct spectra; the first spectrum appears from the commencement of ionisation and consists of a small number of lines, amongst which are the well-known yellow and green lines and a group in the blue. The second spectrum, consisting of a considerable number of lines of which the most intense are situated in the blue and violet, commences to appear at a potential of 28·25 volts and the intensity increases to a maximum at 32—34 volts. The production of the first spectrum corresponds with the ionisation of the neutral atom, but the second spectrum, like the blue spectrum of argon, seems to be produced by several groups of different character. Certain lines result from the double ionisation of the atom, but others are probably emitted by atoms which have lost more than two peripheral electrons. G. F. M.

The Separation of Isotopes. James Kendall and E. D. Crittenden (*Proc. Nat. Acad. Sci.*, 1923, **9**, 75—78).—An outline of two methods by which an attempt is being made to isolate pure isotopes in significant quantity. The ionic migration method is being tested with chlorine- and lithium-ions, the principle of the moving boundary being utilised. Sodium chloride dissolved in agar-agar gel is inserted in the middle horizontal section of a moving boundary tube, and on the two sides of this section are placed, respectively, other sections containing sodium hydroxide and sodium acetate gels. These gels continue up right-angle bends, in which are placed a solution of sodium hydroxide and a solution of sodium acetate in concentrated acetic acid, respectively. On passing a current, the boundaries keep perfectly sharp, and the

conditions are so fixed that they advance 12 to 18 inches a day. When the front chlorine boundary reaches the end of the last section, the apparatus is taken apart, the two rear sections are discarded, and two new sections containing hydroxide gel are fitted in front of the chloride tube. Chlorine-ions are forced to migrate into the two new sections, and the procedure is repeated until the chlorine-ions are passed through 100 ft. of gel. The chloride gel is then cut up into strips. Experiments with sodium iodide and thiocyanate have demonstrated that the front sections contain pure sodium iodide after the gel has moved only a few feet. Thus if the two chlorine-ions possess different mobilities, the faster moving ion should be found in the front section. No separation has been detected in the preliminary experiments, but the work is being continued. The method may be useful in the separation of the elements of the rare earths, and radium from barium.

A discharge potential method of separation is being tested which depends on the different concentration of the two isotopic chlorine-ions. Although it is unlikely that the decomposition potentials of the two isotopes are in any way different, if the Nernst concentration equation holds, the discharge potentials should differ by 0·03 volt. It should therefore be possible to effect an electrolytic fractionation by this means. Chlorine, mercury, magnesium, and lithium are under investigation in this connexion. W. E. G.

Discharge Processes in Gases using Tesla Currents. HERBERT FISCHER (*Z. physikal Chem.*, 1923, **104**, 74—89).—A Tesla current of a maximum voltage of 25,000 has been allowed to pass through air, mixtures of nitrogen and oxygen, and other gases. The results show that oxygen, air, nitrogen, hydrogen, and argon give characteristic colours. The colour exhibited by hydrogen is noteworthy; with a Tesla current of 10,000 volts, hydrogen gives an intense ultramarine colour which after a while becomes greyish-blue. In all cases with oxygen and air, when a current of lower frequency and 9,200 volts is used, ozone is produced, the quantity of ozone increasing almost proportionately with the driving energy of the current. It appears, however, to be possible to increase the yield by increasing the number of plates. With increasing distance between the electrodes the yield of ozone decreases, and it increases with decreasing rate of flow of the gas. Glass and aluminium ozonisers under identical conditions furnish approximately the same concentration of ozone, but ozonisers with a brass electrode furnish extremely small yields of ozone. With Tesla currents, the apparatus becomes heated, so that external cooling becomes necessary. Nitrogen pentoxide is formed in small quantities, but nitrogen trioxide could not be detected. In mixtures of oxygen and nitrogen, the yield of ozone increases with the concentration of the oxygen. J. F. S.

Determination of the Dipole Length of the Hydrogen Chloride Molecule by Electrostriction Experiments. O. E. FRIVOLD and ODD HASSEL (*Physikal. Z.*, 1923, **24**, 82—87).—By

determining the increase of pressure in a dielectric composed of hydrogen chloride, due to charging the plates of a condenser, the authors find that the dipole length of the hydrogen chloride molecule is $0{\cdot}31 \times 10^{-8}$ cm., which is smaller than the value, $0{\cdot}45 \times 10^{-8}$ cm., deduced by Falkenhagen and Weigt (*ibid.*, 1922, **23**, 87) from measurements of the dielectric constant of the gas. The nuclear distance is found to be $1{\cdot}265 \times 10^{-8}$ cm., and the ratio of the two lengths is such that it is impossible to discriminate between the validity or otherwise of the formulæ for the dipole moment deduced, respectively, by Debye and by Pauli on the classical and quantum theories. Such discrimination is possible only when the dipole length is greater than half and less than the whole of the nuclear distance. J. S. G. T.

Recrystallisation of Alloys which Contain a Eutectic. G. Tammann and K. Dahl (*Z. anorg. Chem.*, 1923, **126**, 113—118).—The heating of a wire of a eutectic structure results in a decrease in its electrical resistance. In the case of pure metals, there is a temperature of minimum resistance, but with eutectic wires the minimum resistance is not connected with a definite temperature (cf. Credner, A., 1913, ii, 280). W. T.

Electrical Conductivity of some Gold-Iron Alloys. Examples of the Electrical Behaviour of Limited Mixed Crystal Series. W. Guertler and A. Schulze (*Z. physikal. Chem.*, 1923, **104**, 90—100).—The electrical conductivity of gold-iron alloys containing, respectively, 1, 2, 3, 5, 10, 20, and 40% of gold has been measured at a series of temperatures between 0° and 200°, with the object of testing the validity of Matthiessen's law (1861—1864). This law has been restated in the form that the absolute increase of the resistance on raising the temperature from 0° to 100° is independent of the increase of resistance brought about by the presence of mixed crystals, and has the same value as that calculated from the increase of resistance of the pure components when raised through the same temperature interval, that is, $dW_m/dt = dW/dt$. The experimental results show that the law in the form stated above is entirely true, and that it is not only true over the temperature range 0° to 100°, but also over any other temperature range. It may therefore be also stated in the form that within the range of a given state the differential quotient of the resistance and the temperature, dW/dt, increases in a given series of binary alloys proportionally to the volume concentration of the components. J. F. S.

New Dielectric Constants. Rudolf Keller (*Biochem. Z.*, 1923, **136**, 163—168).—The dielectric constants of a number of physiologically important substances have been determined. They include albumin, pepsin, trypsin, globulin, saliva, and sera. H. K.

The Theory of Electrolytic Ions. XXVIII. The Theory of the Determination of the Limiting Value of the Molecular Conductivity of Strong Electrolytes. Richard Lorenz and A. Landé (*Z. anorg. Chem.*, 1923, **126**, 278—280).—Theoretical.

The authors' experimental formulæ, $1 - x_{K^{\cdot}}/1 - y_{Cl'} =$ constant $= a$; $1 - x_{Na^{\cdot}}/1 - y_{Cl'} =$ constant $= b$; $1 - x_{Na^{\cdot}}/1 - x_{K^{\cdot}} =$ constant $= c = b/a$ (this vol., ii, 9), where x and y are the rates of increase of mobility with dilution of the anion and kation, respectively, are now shown to be generally applicable to binary electrolytes because they can be derived directly from Hertz's law (A., 1912, ii, 120). By a simple mathematical transformation it is shown that for any binary electrolyte the value of $1 - x/1 - y = g^{\cdot}u_0/g'v_0 =$ constant, where $g^{\cdot}$ and g' are constants dependent only on the nature of the ion and not on the concentration, and u_0 and v_0 are the limiting mobilities of the ions. H. H.

The Potentials of Lead-Tin Alloys. S. D. Muzaffar (*Z. anorg. Chem.*, 1923, **126**, 254—256).—From measurements of the potentials of lead-tin alloys of compositions from 0% to 100% tin in potassium hydroxide solution and in a solution of lead acetate in acetic acid, in both of which electrolytes tin is more electropositive than lead, the author concludes that it is highly probable that all these lead-tin alloys contain a complex containing about 9% of tin (cf. A., 1904, ii, 336, 818; 1907, ii, 774, 837). H. H.

Membrane Potentials and Cataphoretic Potentials of Proteins. Jacques Loeb (*J. Gen. Physiol.*, 1923, **5**, 505—519).—A comparison has been made of the membrane potentials of certain protein solutions and the cataphoretic potential difference of protein particles or collodion particles coated with protein, more particularly in respect of the influence of salts. The former potential difference is obtained by measuring the potential difference between the liquids on two sides of a membrane, that on one side containing the protein in solution, the latter from the velocity of the particles under a known potential gradient. Differences exist between the potentials, but in many points there is very marked similarity or identity. It is concluded that in both cases the forces inherent in the protein and linked with the membrane potential act as the determining factor, and that the forces inherent in the water surrounding the particles are secondary, and account for the differences. W. O. K.

An Electrochemical Method of Studying Irreversible Organic Reductions. James B. Conant and Robert E. Lutz (*J. Amer. Chem. Soc.*, 1923, **45**, 1047—1060).—Previous work on reversible reduction of organic substances (this vol., ii, 9) has been extended. The potential of the following combination is measured: Pt|Solution *A* : reducing agent|Solution *A* : quinhydrone|Pt. The material under investigation is then added to the half-cell containing the reducing agent (quinol), and it is noted whether the potential alters during the following thirty minutes. A rise of potential indicates that reduction occurs. In this way, upper potential limits for the reduction of a series of carbonyl derivatives of ethylene have been determined, in acetone and alcoholic solutions. The results show that the potential at which the substance is irreversibly reduced is approximately proportional to the reactivity

of the carbonyl group. The reduction of nitrosobenzene to phenylhydroxylamine is shown to be reversible, and the potential is measured. Preliminary values are given for a series of nitrogen compounds, which are irreversibly reduced.

A theory of irreversible reductions is advanced which qualitatively connects the "apparent reduction potential" with a true oxidation-reduction potential of the substance in question. W. S. N.

Concentration Cells in Non-aqueous Solvents. A. N. Sachanov and A. M. Grinbaum (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1794—1806).—The *E.M.F.* of concentration cells of silver nitrate in pyridine solution is investigated; it is for very small concentrations of silver nitrate (from $0{\cdot}01N$ to $0{\cdot}0004N$) little different from that calculated by Nernst's theory, or obtained with aqueous solutions. With greater concentrations, wide variations from theory are observed, due to the formation of complex kations and to anomalous dissociation. The degree of dissociation of silver nitrate in pyridine solution is calculated, and found to decrease rapidly as the concentration becomes greater than $0{\cdot}1N$. Minimum dissociation occurs with a normal solution, whilst at higher concentrations the degree of dissociation again increases owing to anomalies in dissociation. R. T.

Action of Gelatin on Concentration Cells. René Audubert (*Compt. rend.*, 1923, **176**, 838—840).—The addition of gelatin to the concentration cells $AgI-AgNO_3$, $AgCl-AgNO_3$, and $Ag_2S-AgNO_3$ caused a diminution of the electromotive force when it was added to the silver nitrate solution, and an increase when the addition was made in the neighbourhood of the other electrode. The action of the gelatin is therefore to diminish the concentration of silver-ions, and given that $\epsilon = RT/96600LC/c$, where C is the concentration of silver-ions in the nitrate solution, and c that of the same ions at the other electrode, a measurement of ϵ with and without the addition of gelatin is all that is required to give the diminution in concentration of the silver-ions caused by the addition of varying amounts of gelatin, by substitution in the expression $C - C' = c[e96600\epsilon/RT - e96600\epsilon'/RT]$. The determinations showed that the quantity of ions fixed by the gelatin was a continuous function of the concentration C' of the ions in equilibrium with the colloid, which could be expressed as $C - C' = AC'^p$, where p is a coefficient independent of the concentration of the gelatin and of the nature of the cell. Its value approximated to $0{\cdot}5$, showing that the formula given by Freundlich to represent an adsorption isotherm can be applied to the equilibrium between the silver-ions and the gelatin. It seems therefore that the silver-ion forms an adsorption complex with the gelatin. The influence exercised by gelatin in the formation of a fine electrolytic deposit can be attributed to an increased cathodic polarisation. G. F. M.

Bimetallic Electrode System Applied to Neutralisation Reactions. H. H. Willard and Florence Fenwick (*J. Amer. Chem. Soc.*, 1923, **45**, 715—716).—In an attempt to use bimetallic

electrode systems in neutralisation reactions, it was found that the electrodes reacted very sluggishly in the region of the neutral point. The addition of potassium bromate to the solution did not improve matters, but on the addition of neutral hydrogen peroxide the electrodes regained their normal activity and retained it up to the neutral point. A potential difference persisted up to 0·3—0·4 c.c. of 0·1N-titrating solution of the end-point, it then began to decrease and at the neutral point a clear, sharp, downward break occurred. With the reversed titration, a rise preceded the end-point, which was marked by a break upwards of about 100 mv. In both cases, the point of the maximum velocity of potential change is exactly coincident with the "green point" of bromothymolsulphonephthalein, which corresponds with a P_H value of 6·8. In neither case was the end-point permanent. Rapid stirring of the solution favoured the absorption of carbon dioxide to such an extent that variable results were obtained in consecutive titrations approaching the neutral point from the alkaline side. With the approach on the opposite side the crawl as the end-point was passed is not sufficient to impair seriously the clarity of the break. The method appears to offer possibilities for the development of a new type of hydrogen electrode which is unique in its independence of an external gas supply. J. F. S.

Electrolytic Dissociation of Water in Salt Solutions. E. LINDE (*Z. Elektrochem.*, 1923, 29, 163—168).—The respective viscosities of solutions of lithium chloride and calcium chloride of various concentrations up to saturation (44·1% and 46·4%, respectively), at 25°, have been determined, and the results indicate that the product of viscosity and electrical conductivity in each case increases continuously with increase of concentration of the solutions. Values of the viscosities determined have been applied to correct the values found by Palmaer and Melander (A., 1915, ii, 727) for the *E.M.F.* of hydrogen electrodes in aqueous solutions of lithium chloride and calcium chloride of various concentrations, such correction being necessary owing to the contact difference of potential between the two solutions employed, arising from a difference in their viscosities. Corresponding values of normality and corrected *E.M.F.* for lithium chloride solutions at 22° are: 1·5N, 0·124; 1·8N, 0·127; 3·0N, 0·115; 5·7N, 0·112; 7·2N, 0·052 volt. In the case of solutions of calcium chloride at 25·5°, corrected values were determined as follows: 0·65N, 0·168; 1·50N, 0·131; 2·18N, 0·098; 2·50N, 0·106; 4·00N, 0·053; 5·07N, 0·038 volt. The respective relative concentrations of hydrogen-ions in the various solutions are calculated from the corrected values of *E.M.F.* by Nernst's formula. J. S. G. T.

The Electrochemistry of Non-aqueous Solutions. III. Electrolytic Deposition of Alkali Metals from Solutions in Anhydrous Pyridine. ROBERT MÜLLER, F. HÖLZL, A. PONTONI, and O. WINTERSTEINER (*Monatsh.*, 1923, 43, 419—437; cf. A., 1922, ii, 612; Kahlenberg, A., 1900, ii, 521, and Patten and Mott, A., 1908, ii, 253).—Previous work is continued, the standard

electrode already described being used for measurements; in the following, potentials are referred to the electrode Ag|0·1NAgNO$_3$ in pyridine =0, unless otherwise indicated. The decomposition potentials for 0·1N, N, and saturated solutions of lithium chloride in pyridine are, respectively, 4·18, 4·05, and 4·05 volts. With a mercury cathode, the three solutions give the same value, −2·83 volts. The deposition potential of lithium (NLiCl solution) is 3·1 volts (E_p=2·82 volts), the corresponding anodic potential being 0·85 volt (E_p=1·3 volts). Using a more delicate electrometer, the following results were obtained: Lithium potentials for saturated and N-lithium chloride solutions are, respectively, 3·09 and 3·12 volts. The corresponding anodic potentials are 0·73 and 0·74 volt. For N-lithium chloride, the lithium potential referred to the hydrogen electrode is 2·83 volts. The decomposition potentials varied from 3·8 to 3·9 volts (values of deposition potential are obtained in all cases by producing the straight portion of the polarisation curves downwards, to meet the potential axis).

The presence of water in N-lithium chloride (pyridine) solutions gives rise to totally different cathodic and anodic polarisation curves, probably owing to the separation of lithium hydroxide (see Patten and Mott, *loc. cit.*).

The cell, Li|LiCl|0·1NAgNO$_3$|Ag, has E 3·16 and 3·2 volts for N and 0·1N-lithium chloride, respectively.

Similar measurements with lithium nitrate gave: Cathodic potentials, 2·00 and 1·90 volts, anodic potentials, 3·06 and 3·09 volts for saturated and N-lithium nitrate, respectively. Decomposition potentials (for saturated solution) 5·01 volts. The cell Li|LiNO$_3$|0·1NAgNO$_3$|Ag has E 2·86, 3·05, 3·10, and 3·15 volts for the four concentrations, saturated, N-, 0·1N-, and 0·01N-lithium nitrate (in pyridine), respectively.

Sodium is not deposited from sodium iodide–pyridine solutions under conditions similar to those used in the case of lithium. With sodium thiocyanate no definite polarisation figures were obtainable. Emmert's dipyridine sodium (A., 1921, i, 268) may be responsible for these irregularities. The anodic polarisation in each case was more definite. Sodium nitrate solutions conducted too badly to allow of their investigation.

With potassium thiocyanate, one of the few potassium salts soluble in pyridine, no separation of metal occurred on a platinum electrode, but, using a mercury cathode, separation occurred readily and the constant potential of 1·77 volts was observed, the corresponding potential for the anode being 0·42 volt. The cell K|KCNS(saturated solution)|0·1NAgNO$_3$|Ag gave 2·58 volts.

E. E. T.

A New Method to Determine the Hydration of Ions. The Hydration of the Lithium-ion. GEORGE BABOROVSKÝ (*Rec. trav. chim.*, 1923, **42**, 229—239).—The author describes a new form of apparatus for determining the transport number and hydration of ions, and gives the results of a series of experiments carried out with solutions of lithium chloride. The value for the hydration

of the lithium-ion was found by determining the change in mass and concentration of the electrode solutions and shows that the ion adds one molecule of water assuming that the hydration of the chlorine-ion is zero. The transport number of the lithium-ion in decinormal solution of the chloride is 0.3128 ± 0.0048. H. J. E.

The Ionising Power of Molten Lithium Hydride. A. GUNTZ and BENOIT (*Compt. rend.*, 1923, **176**, 970—971).—The electrolysis of the solution of lithium carbide in molten lithium hydride obtained by the action of lithium on ethylene results in a separation of carbon at the anode. This is not due to the action of hydrogen on the carbide, which only occurs above 600°, and it is concluded that the carbide is ionised in the molten hydride. It was found that no hydrogen was evolved at the anode with a voltage below 0·1, whilst deposition of carbon occurred at 0·05 volt. Similar results were obtained with solutions of calcium carbide in lithium or calcium hydride, or a mixture of lithium or calcium hydride and chloride. The nitrides of the alkaline-earth metals are also soluble in the corresponding hydrides, and appear to be ionised in a similar way. G. F. M.

The Formation of a Reducing Substance at the Cathode by the Electrolysis of Acid and Alkaline Solutions. G. TAMMANN (*Z. anorg. Chem.*, 1923, **126**, 176—178).—The cathode liquid after the electrolysis of a dilute solution of sodium or potassium hydroxide or sulphuric acid has the property of reducing an alkaline solution of silver. The reducing agent is unstable, and one-half of it disappears in one day. It is shown that this reduction cannot be due to the presence of ferrous hydroxide or to active hydrogen (H_3). Attempts were made to extract the reducing agent with benzene, the benzene solution being then shaken with hydrochloric acid; the concentration of the substance was found to have thus increased tenfold. The author does not speculate as to the nature of the substance, pure specimens of which could not be obtained. W. T.

The Electrophoresis of Chromic Solutions. F. L. SEYMOUR-JONES (*Ind. Eng. Chem.*, 1923, **15**, 265—266).—Thompson and Atkin have recently suggested (*J. Soc. Leather Trades Chem.*, 1922, **6**, 267) that in chrome liquors used in tanning, the active tanning agent is a negatively charged chromium complex, but electrophoresis experiments on normal and basic solutions of chromic chloride and sulphate and of chrome alum showed that anodic migration of chromium occurs only in basic sulphate solutions, and therefore no such negative complex can exist in solutions of the chloride or of chrome alum. Since, however, basic chloride solutions tan hide powder in a perfectly normal fashion, the theory that a negatively charged chromium complex is always the active tanning agent cannot be maintained. G. F. M.

The Magneto-chemical Effect. A. N. SCHTSCHUKAREV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1785—1793).—Barium chloride solution is electrolysed in a strong magnetic field. A stream of positively charged particles is observed to emanate from the region

of the solution where liberation of ions take place. These particles move with great velocity, as they are able to penetrate a layer of solution 1 cm. in thickness, the minimum penetrative power observed being half as great. The nature of these particles is not certain, but it seems possible that they are produced as a result of the disintegration of the chlorine atom. A platinum-platino-iridium thermo-element placed in the solution within range of the particles gives a perceptible heat effect, so that they appear to possess considerable kinetic energy. A stream of negatively charged particles is also observed, but these have not up to the present been investigated. R. T.

A New Method for the Control of Thermostats. D. J. Beaver and J. J. Beaver (*Ind. Eng. Chem.*, 1923, **15**, 359—361).—An apparatus is described by means of which it is possible to maintain water or oil thermostats of capacities of 10—300 litres constant to 0·001° over long periods of time with little attention. Sparking at the mercury contact which causes surface oxidation of the metal is eliminated by using a very small current across the contact, and amplifying it sufficiently by means of a vacuum tube to actuate a magnetic relay or other current controlling mechanism. With a 120 volt direct current supply, and a resistance of 1 megohm between the grid of the vacuum tube and the mercury contact, the current across the latter is approximately 2×10^{-5} amperes, which is far too small to produce an arc at the contact surface. When the thermoregulator is not fastened rigidly to the thermostat, the mercury surface oscillates rapidly. This increases the sensitiveness of regulation, but it is desirable to slow the oscillation down to a frequency of about 2 per second by placing a condenser of 0·1 microfarad capacity in parallel with the resistance between the grid and the filament. The thermoregulator consists of a glass spiral filled with toluene or turpentine, to the upper end of which a capillary U-tube of 1·5 mm. bore is sealed. This is filled with mercury, and a platinum wire sealed in the lower part of the U-tube is used to make one contact, whilst a fine iron or nickel wire makes the adjustable contact in the capillary. Back lash at the mercury contact is thus eliminated as neither of these metals is wetted by the mercury. A Monel metal tube charged with mercury provides a more sensitive regulator, and should be used if the room temperature is liable to fluctuate 5° or more from the bath temperature. G. F. M.

The Heat of Vaporisation and the Difference in the Specific Heats of the Saturated Vapour and of the Liquid States for Neon. E. Mathias, C. A. Crommelin, and H. Kamerlingh Onnes (*Compt. rend.*, 1923, **176**, 939—940).—The latent heat of vaporisation of neon was calculated from the Clapeyron-Clausius formula $L=T/J(1/\delta'-1/\delta)dp/dT$, the densities δ and δ' of the liquid and saturated vapour at $T°$ and a pressure p being obtained from earlier work (A., 1922, ii, 472). The values found for L as a function of the temperature are closely expressed by the equation $L^2=43{\cdot}56922(T_c-T)-1{\cdot}744347(T_c-T)^2+0{\cdot}0371203(T_c-T)^3$, where

T_c is the absolute critical temperature. The difference in the specific heats of the liquid m, and the saturated vapour m' was then obtained from the equation $m'-m=dL/dT-L/T$. The value was strongly negative at the critical point, and remains negative at all temperatures, with a maximum at a temperature $T/T_c=0{\cdot}74$. The values found for neon at a temperature $T/T_c=0{\cdot}6$ were as follows: T_c 44·38°, L 20·8, ML 420, and $L\Delta/p_c$ 0·374, where ML is the molecular heat of vaporisation, Δ the critical density, and p_c the critical pressure. A comparison with the corresponding values for oxygen, argon, nitrogen, and hydrogen shows that the deviations from the law of corresponding states increase as the critical temperature decreases. G. F. M.

Relation between the Dipole Moment and Heat of Sublimation of the Hydrogen Halides. M. BORN and H. KORNFELD (*Physikal. Z.*, 1923, **24**, 121—124).—The authors suggest that crystals of the hydrogen halides are built up of cubical crystal lattices, the unit cube of the lattice consisting of two congruent regular tetrahedra, at the corners of which molecular dipoles having their positive poles directed respectively towards and away from the centre of the cube are arranged. By considering the attractive and repulsive forces arising from such an arrangement of dipoles, an expression is deduced for the heat of sublimation of the respective halides, in the form $S=1{\cdot}565\times10^{40}p^2d/M$, where S is the heat of sublimation, p the dipole moment, d the density, and M the molecular weight of the respective halides. Values of the dipole moment calculated from the respective heats of sublimation by means of this equation are: HCl, $2{\cdot}90\times10^{-18}$; HBr, $3{\cdot}35\times10^{-18}$; and HI, $3{\cdot}89\times10^{-18}$. Frivold and Hassel (this vol., ii, 283) found $1{\cdot}48\times10^{-18}$, and Falkenhagen and Weigt $2{\cdot}15\times10^{-18}$ for the dipole moment of HCl. The calculated values for HCl and HBr are respectively half those calculated from the experimental values of Kratzer for the nuclear distances in the two cases, and constitute an upper limit in each case. It is shown that values of the respective heats of ionisation of HCl and HBr calculated by means of the formula $2{\cdot}388\times10^{-11}N.e^2(1+4s/r_0)/r_0$ where N is the appropriate Loschmidt number, r_0 the nuclear distance, s the distance between the centre of gravity of the outer electrons of the halogen and the core, and e has the customary significance agree very closely with the experimental values found by Knipping (A., 1922, ii, 186). J. S. G. T.

Vapour Pressure of Copper Oxide and of Copper. EDWARD MACK, GERARD G. OSTERHOF, and HOBART M. KRANER (*J. Amer. Chem. Soc.*, 1923, **45**, 617—623).—The vapour pressure of copper and copper oxide has been determined by the dynamic method. A stream of nitrogen was led over the heated copper and passed into water which removed the whole of the copper vapour; in the case of the oxide oxygen was used instead of nitrogen. The amount of copper in the water was estimated by measuring the acceleration in the rate of oxidation of sodium sulphite by dissolved oxygen brought about by the copper in the water (Titof,

A., 1904, ii, 113). The following values of the vapour pressure are recorded: copper oxide, 600°, 10^{-7} mm.; 800°, 10^{-4} mm.; 900°, 7×10^{-4} mm., and 1000°, 10^{-4} mm.; copper, 810°, 5×10^{-7} mm. The value for copper oxide at 1000° does not represent a true vapour pressure for this substance, for at this temperature the vapour is a mixture of cupric and cuprous oxides. The heat of vaporisation of cupric oxide over the temperature range 600—800° has been calculated, and the value 63,000 cal. obtained. The present results have been compared with those of other workers and a satisfactory agreement has been found. J. F. S.

Vapour Pressures of certain Hydrated Metal Sulphates. CLIFFORD D. CARPENTER and ERIC R. JETTE (*J. Amer. Chem. Soc.*, 1923, **45**, 578—590).—The vapour pressure of the tri- and penta-hydrates of copper sulphate, the heptahydrate of magnesium sulphate, the eight-thirds hydrate of cadmium sulphate, the heptahydrate of cobalt sulphate, and the monohydrate of manganese sulphate has been determined at a series of temperatures by the static method. A Bremer-Frowein tensimeter of modified structure has been used in the work, which is described together with manipulative details necessary to eliminate the usual errors. In all determinations, the value was reached from both sides. The vapour pressures of the saturated solutions of some of the hydrates have also been determined at 20—90°. A new transition point has been found for the heptahydrate of cobalt sulphate at 45·1°, and for the eight-thirds hydrate of cadmium sulphate at 41·5°. The transition point for the change from the heptahydrate of magnesium sulphate to the hexahydrate is found to lie at 48·4°; this point was previously found by van der Heide (A., 1894, ii, 92) to lie between 48·0° and 48·5°. The heat of the reaction $AB.xH_2O+H_2O \rightleftharpoons AB.(1+x)H_2O+Qp$ has been calculated in each case, where Qp is given by the relation $Qp=RT^2.d\log_e p/dT$, so that Qp is therefore the heat of reaction per mol. of water at constant pressure. The average values of Q are $CuSO_4,3H_2O$, 13256; $CuSO_4,5H_2O$, 13268; $CdSO_4,8/3H_2O$, 11170; $MgSO_4,7H_2O$, 14035; $MgSO_4,6H_2O$ (saturated solution), 9741; $CoSO_4,7H_2O$, 12795; and $CoSO_4,6H_2O$ (saturated solution), 9760. The value of Q usually changes most abruptly at the transition point, and it is nearly constant as long as the same phases are present. On account of this fact, most transition points are readily found by the intersection of the lines drawn through the points determined by the $\log p$ and $1/T$ relationship. J. F. S.

The Vapour Pressures of Saturated Solutions of Alums. STANISLAV MACISCHEVSKI (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1916—1923).—The vapour-pressure curves for potassium and ammonium alums are plotted, in order to see whether the empirical formula of Speranski (A., 1913, ii, 923) connecting vapour pressure, temperature, and concentration of solutions is applicable to double salts. These curves consist each of two curves, intersecting, in the case of potassium alum at 79·5° and in the case of ammonium alum, at 82·7, indicating that at these points chemical change of

the alums occurs. Bertrand's formula connecting vapour pressure and temperature is not applicable to the curves for these two alums as a whole, but only to each portion separately. Speranski's formula is not applicable to the potassium alum curve, and is only applicable to the ammonium alum curve below 82·7°. R. T.

The Form of the Vapour-pressure Curve at High Temperatures. II. The Curve for Sodium Cyanide. CHRISTOPHER KELK INGOLD (T., 1923, **123**, 885—891).

Relationship between the Properties of Liquid Substances. W. HERZ (*Z. Elektrochem.*, 1923, **29**, 110—111).—An equation has been deduced from the revised Trouton rule and the Clausius-Clapeyron vapour-pressure formula which gives a connexion between the boiling point of a liquid and its vapour pressure at a given temperature. This equation has the form $\log p_1 = \log 760 - (9{\cdot}5 \log T_s - 0{\cdot}007T_s)(T_s - T_1)/4{\cdot}57T_1$, where p_1 is the vapour pressure at the temperature T_1 and T_s the boiling point of the liquid. The agreement between the calculated and experimentally determined vapour pressure, whilst moderately good, is not sufficiently near to make the formula trustworthy for the calculation of vapour pressures. With liquids of medium boiling point which are not associated, the surface tension at the boiling point can be calculated from the density at the boiling point and the molecular weight by the formula $\gamma = T_s S^{2/3}(9{\cdot}5 \log T_s - 0{\cdot}007T_s)/20M^{2/3}$, where M is the molecular weight, and S the density at the boiling point. The calculated results are sufficiently near the experimental values except in the case of carbon disulphide, where the two values differ by about 30%. The gas constant can also be calculated approximately from the boiling point by the formula $R = 3875(9{\cdot}5 \log T_s - 0{\cdot}007T_s)$. The calculated results are from 15—20% higher than the true value. J. F. S.

The Determination of Boiling Points by Distillation from Test-tubes. A. K. BOLDYREV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1862—1870).—A slight modification of the method described by Pawlewski (A., 1881, 642) for the determination of the boiling point of small quantities of substances. A small test-tube, provided with a side-tube, and a cork through which a thermometer passes, is wrapped round with asbestos, and fits into an aperture cut in a sheet of the same material. The lower end of the tube which protrudes through the asbestos sheet is heated with a naked flame until the contents boil. The thermometer reading at first rises, then remains constant for some time, this temperature being taken as the boiling point, and then again rises, owing to superheating. The best results are obtained by keeping the bulb of the thermometer at least 4 cm. above the level of the liquid, so as to avoid the spattering of the superheated liquid. By this method triphenylamine gave b. p. 364·8° (corr.). Its solubility in 100 g. of ethyl and of methyl alcohol is measured, and is in the former solvent 0·74 g. at 19—20·5°, and 5·5 g. at 74°, and for the latter 0·73 g. at 19—20·5°, and 3·3 g. at 65°. R. T.

Distillation of Small Quantities of Liquids. FRANZ LANYAR and LUDWIG ZECHNER (*Monatsh.*, 1923, **43**, 405—412).—Fractional distillation of small quantities (1 to 3 drops) of liquid mixtures is readily effected, using a glass tube 50—60 mm. long and 5—8 mm. wide, sealed at one end, and constricted once or twice near the open end. The liquid (absorbed by a little asbestos wool at the closed end) may be separated, by careful heating with a micro-burner, into as many as ten fractions, which are drawn successively into capillary tubes suitable for b. p. determinations. Eleven separations effected in this manner show that the method is capable of general application. E. E. T.

A Laboratory Fractionating Column. H. T. CLARKE and E. J. RAHRS (*Ind. Eng. Chem.*, 1923, **15**, 349).—The column consists of a Pyrex tube 90 cm. long and 20 mm. in diameter, having a series of semi-bulbs sucked in, beginning 15 cm. from the top and arranged at an angle of 90° on the periphery of the tube. Opposite each bulb a point is poked in to within 1 mm. of the upper part of the inner convex surface of the bulb. At 8 cm. from the upper end of the column a side arm is fused in, similar to that of a Claisen flask, and the delivery tube situated at the mid-point of its vertical portion is bent so as to ascend for a short distance before descending to the condenser. At the top of the column is fixed a Pyrex tube 16 cm. long and 15 mm. diameter through which cold water can be circulated, and the entire length of the column below the side arm to within 8 cm. of the lower end is jacketed with a glass tube, tubulated at each end, and secured by rubber stoppers. The position of the water-cooled tube is adjusted to suit the boiling point of the liquid which is being distilled so that 10 to 15 times as much condensate is returned to the flask as collects in the receiver. For very low boiling liquids, the jacket may be filled with water, or cold air drawn through at a regulated rate. For high boiling liquids, the tubulations are closed so that the jacket acts as a heat insulator. G. F. M.

Calorimetric Researches. IV. Determination of the Heat of Combustion of Sucrose; Suitability of this Substance as a Thermochemical Standard. P. E. VERKADE and J. COOPS, jun. (*Rec. trav. chim.*, 1923, **42**, 205—228; cf. P. E. Verkade, A., 1922, ii, 740).—The authors consider that a second standard substance is necessary for thermochemical work and give reasons for testing sucrose as a possible substitute for naphthalene. As a result of a series of experiments, the ratio of the heat of combustion of benzoic acid to that of sucrose was found to be 1·6025 (air), the corresponding figure for naphthalene and sucrose being 2·4362 (air). In a review of the various objections which have been raised to the use of sucrose, the reasons in favour of using that substance are adduced but the tendency to incomplete combustion and the difficulty of ignition cannot be obviated. The conclusion is drawn that none of the substances hitherto investigated is quite satisfactory as a secondary standard. The values obtained for sucrose, on the assumption that the heat of combustion of

benzoic acid is 6324 cal.$_{15}$, per g. (air), are 3946 (air) and 3944 (vacuum). H. J. E.

The Variation of Heats of Solution with the Temperature. PAUL MONDAIN-MONVAL (*Compt. rend.*, 1923, **176**, 889—892).—In order to demonstrate the influence of temperature on the heat effects of solution, dilution, etc., the following measurements were made at 0° and at the ordinary temperature of the heats of solution, etc., of sodium, potassium, and ammonium nitrates, potassium and ammonium chlorides, and potassium sulphate: molecular heat of solution in a large quantity of water, Q; heat absorbed by dilution of the saturated solution to the above dilution, D; heat of addition of 1 mol. H_2O to a large quantity of saturated solution, E'; and heat of addition of a quantity of water sufficient to dissolve at saturation 1 mol. of the salt, E. L_1 representing the heat limit of solution in saturated solution, was calculated from the relation $L_1=Q-D-E$, and as a check on the result the same quantity was obtained by a slight extrapolation of the experimental results obtained by the direct solution of the salt in solutions of increasing concentration. The complete results are given in tabular form, and they show in all cases a distinct difference in the values obtained at 0° and at the ordinary temperature (18—19°). G. F. M.

Dilatometric Researches on Potassium Aluminium Sulphate. (MLLE) E. N. IVANOVA (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1905—1916).—It was noticed by Wiedeman (A., 1883, 780) that potassium alum contracts when heated above 51·3° in a dilatometer, and he explains this as being due to dissociation of the constituent molecules of the alum. This experiment was repeated, but no contraction was observed up to 87·3°, using either mercury or paraffin as the dilatometer liquid. The contraction observed by Wiedeman was probably due to the slow filling up of the interstices of the powdered alum by mercury. The use of paraffin above 75° is not recommended, as expansion of air adsorbed on the solid causes an abnormal expansion in the dilatometer. This adsorbed air is very difficult to eliminate. R. T.

Force of Adhesion in Solutions. IV. Influence of Temperature on the Partition of Substances between two Phases. SERG. WOSNESSENSKI (*Z. physikal. Chem.*, 1923, **104**, 46—50).—A theoretical paper, in which, on the basis of Schilov and Lepin's work on the adsorption of substances by charcoal (A., 1920, ii, 591; 1922, ii, 626) and Iljin's theoretically deduced formula for the influence of temperature on the adsorption equilibrium (*Nachr. Moskauer physik-wiss. Inst.*, **1**, 219), the author has examined his previously published adsorption results and those of other authors. The calculated results show that the experimental values for the partition of succinic acid between ether and water, benzoic acid between benzene and water, ferric thiocyanate between water and ether, the adsorption of physiological salt solution by animal membrane and the adsorption of water by beans, are all in agree-

ment with the values calculated by Iljin's formula, $C_\infty = C_0 e^{t}$ thus showing that the essential process is the same in all cases.
J. F. S.

Adsorption of Gases by Solids and the Thickness of the Adsorbed Layer. M. H. Evans and H. J. George (*Proc. Roy. Soc.*, 1923, [*A*], **103**, 190—193).—By direct determination, the authors find the thickness of the adsorbed layer of carbon dioxide on glass fibres having an average area of $9 \cdot 093 \times 10^2$ sq. cm. per g. to be equivalent to that of 5·5 molecular layers, assuming the adsorbed gas to exist as a film having the density of liquid carbon dioxide. The equilibrium pressure was found to be 121·46 mm., and using Mülfarth's data (*Ann. Physik*, 1900, [iv], **3**, 328) for relative adsorption at 0° and at this pressure, the following results were calculated for the respective thicknesses of the adsorbed layer for the following gases: sulphur dioxide, 32·1; ammonia, 39·9; nitrous oxide, 4·5; acetylene, 3·5 molecular layers. These values are considerably greater than the values, not greater than the diameter of a single molecule, required by Langmuir's theory (A., 1918, ii, 430), and deduced from experiments with gases at low pressures.
J. S. G. T.

A Case of Simultaneous Positive and Negative Adsorption. M. A. Rakuzin and (Mlle) G. F. Pekarskaja (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1889—1890).—The adsorption of Bismarck-brown by gelatin and by leather powder is found to consist of both positive and negative adsorption. The increase in the concentration of the solution, owing to adsorption of water, shows the latter, whilst the former is shown by the decolorisation of the solution. An increase in the optical rotation of the solution from 0° to +0·55° in the case of gelatin shows that some of the latter passes into solution.
R. T.

Sorption Equilibria. H. von Euler and Birger Bucht (*Z. anorg. Chem.*, 1923, **126**, 269—277).—The solubility of casein in aqueous and alcoholic solutions of monochloroacetic acid, and in alcoholic and benzene solutions of α-bromopropionic acid is measured. The corresponding sorptions of acid by the undissolved casein are also measured, and it is shown that the amount of acid sorbed per gram of casein is a linear function of the concentration of acid in the solution.

An attempt was made to obtain an asymmetric sorption of α-bromopropionic acid from benzene solution, but although in the most favourable experiment 0·64 g. of casein sorbed 0·555 g. of the acid from a solution containing 1·418 g., no optical activity was detected in the residual solution, and the authors draw the conclusion that any asymmetric sorption cannot exceed 10% of the whole.
H. H.

Dissociation of Molecular Hydrogen, [Deduced] from the Entropies of Diatomic and Monatomic Hydrogen. Graham Edgar (*J. Amer. Chem. Soc.*, 1923, **45**, 673—676).—A theoretical paper in which the free energy of dissociation, the dissociation constant, and

the degree of dissociation of molecular hydrogen have been calculated from the entropies of the substances and published data for the heat of dissociation. Tables are given of the values of the entropy, heats of reaction, and the equilibrium constants for 298·1° 1500°, 2000°, 2500°, and 3000° Abs., and a further table showing the fraction of hydrogen dissociated at the four higher temperatures at pressures 1, 0·1, and 0·001 atm. The results indicate, in keeping with the conclusions of Duffenback (A., 1922, ii, 620) and Saha (A., 1920, ii, 659), that hydrogen is much more dissociated at high temperatures than earlier calculations indicated. The following values of the fraction dissociated at 1 atm. pressure and various temperatures are recorded: 1500°, 0·000316; 2000°, 0·0063; 2500°, 0·0595, and 3000°, 0·26. J. F. S.

Velocity of Sound in Nitrogen Peroxide. HERMANN SELLE (*Z. physikal. Chem.*, 1923, **104**, 1—9).—The velocity of sound in nitrogen peroxide has been determined at various pressures and temperatures by both the Kundt and Clément and Desormes methods. It is shown that there is a dispersion of sound in the region of vibration numbers 3670 to 1690. With decreasing vibration number this value sinks to about 3 m./sec. Sound dispersion is shown at the various temperatures and pressures investigated. Using the Clément and Desormes method, the values of $k=Cp/C_v$ and $\sqrt{\Delta p/\Delta\rho}$ were determined. This furnishes the velocity of sound for very slow vibrations. Taking account of this value, the sound dispersion at 21° and 500 mm. pressure is 4 m./sec. or 2·2% of the velocity. From the relationship between the velocity of sound and the course of the reaction $2NO_2 \rightleftharpoons N_2O_4$, the proportionality factors k_1 and k_2 were determined. Between 18° and 26°, the value of k_1 increases with the temperature from 376 to 617; in the case of k_2, $4·8\times10^6$ is found as a mean value, and no dependence of this value on temperature was observed. A dependence on pressure was not found for either k_1 or k_2. According to these determinations, 1 g.-mol. of N_2O_4 at 21° and 500 mm. pressure dissociates to the extent of 4·4% in 10^{-4} secs., and 1 g.-mol. of pure NO_2 associates to the extent of 4·6% to N_2O_4 in 10^{-8} secs. J. F. S.

Theory of the Capillary Layer of a Liquid in Contact with its Saturated Vapour. G. BAKKER (*Z. physikal. Chem.*, 1923, **104**, 10—45).—A general discussion of the theory of the capillary layer as previously published (A., 1903, ii, 62; 1904, ii, 310, 540, 655, 806; 1905, ii, 304; 1910, ii, 106, 831; 1912, ii, 743; 1916, ii, 553). J. F. S.

Separation of Gas Mixtures by Diffusion in a Flowing Gas. G. HERTZ (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **25**, 434—441).—When a gaseous mixture diffuses into a medium at rest the ratio of the partial pressures of the components of the mixture is constant, but if the mixture of gases diffuses into a medium in motion, the ratio of the partial pressures of the constituents is variable and this fact offers possibilities for the separation of the

constituents of gaseous mixtures. Equations are deduced showing the amount of separation which may be brought about by diffusion into a moving medium. The method has been applied to the case of mixtures of neon and helium. A jet of steam was allowed to enter a vessel containing the gas mixture through a number of narrow holes, a portion of the gas diffused through the holes against the steam jet and was pumped off, the steam was condensed after it entered the vessel, and so two fractions of gas were obtained. Using a 30% helium 70% neon mixture, pure helium was obtained by a single treatment. The separation was in accordance with the theory, but the amount of gas thus separated was small. Methods of increasing the amount separated are discussed, and the principle is also discussed generally in connexion with the separation of isotopes. It is shown that in the case of neon a separation of the isotopes to the extent of 30% may be expected from a single treatment. J. F. S.

Anomalous Osmosis of Solutions of Electrolytes with Collodion Membranes. II. Effect of the Diameter of the Pores. F. E. BARTELL and D. C. CARPENTER (*J. Physical Chem.*, 1923, **27**, 252—269; cf. this vol., ii, 221).—The influence of the size of the pores of collodion membranes on the rate of osmosis has been investigated. It is shown that the rate at which solutions of potassium ferricyanide and aluminium chloride pass through a collodion membrane increases at all concentrations as the diameter of the pores increases. On the other hand, the relative diffusion values of potassium sulphate and calcium chloride decreases materially with increasing diameter of the pores. The rate of diffusion of solutions of potassium chloride remains approximately constant with the various membranes. In dilute solutions, potassium sulphate, calcium chloride, and aluminium chloride appear to pass through the membrane at a greater rate than the other salts. Comparisons of the rate of passage of potassium salts through the least porous membranes, that is, membranes with pores of diameter about 0·7 micron, in the case of dilute solutions gave the following anion order: $SO_4'' > Cl' > Fe(CN)_6'''$. For concentrated solutions, the order for a similar membrane was $Cl' > SO_4'' > Fe(CN)_6'''$. The latter order is the inverse of the order of magnitude of maximum osmosis. Comparisons of the rates of passage of chlorides into water showed the kation order in dilute solution to be $Al^{\cdot\cdot\cdot} > Ca^{\cdot\cdot} > K^{\cdot}$. Exactly the opposite order was found for concentrated solutions. The order of magnitude of osmosis with dilute solutions bears no apparent relation to the kation diffusion order; however, the order of magnitude of osmosis with concentrated solutions was the inverse of the kation diffusion order. With membranes of pore diameter about 0·93 micron, the anion order for the rate of diffusion of potassium salts from dilute solutions was $SO_4'' > Cl' > Fe(CN)_6'''$, and with concentrated solutions $Cl' > SO_4'' > Fe(CN)_6'''$. This was again the inverse of the maximum osmosis for concentrated solutions. The kation order for the rate of diffusion is $Ca^{\cdot\cdot} > K^{\cdot} > Al^{\cdot\cdot\cdot}$ in dilute solutions and $Ca^{\cdot\cdot} > Al^{\cdot\cdot\cdot} > K^{\cdot}$

in concentrated solutions. For very permeable membranes of pore diameter 1·6 microns, comparison of the amounts of potassium salts diffusing during the period of maximum osmosis gave the order for anions $Cl' > SO_4'' > Fe(CN)_6'''$ for both dilute and concentrated solutions. This order is the inverse of that of maximum osmosis. For chlorides, the kation order is $K^{\cdot} > Ca^{\cdot\cdot} > Al^{\cdot\cdot\cdot}$ in all solutions. This order is the same as that of maximum osmosis in very dilute solutions, but the reverse of that in concentrated solutions. The work shows generally that the diameter of the pores is a highly important factor in determining the exact nature of osmosis, and it appears probable that the phenomena of anomalous osmosis and the attending salt diffusion is governed largely by the precise diameter of the pores of the osmotic membrane.

J. F. S.

Electroendosmosis through Carbon Filters. Kojiro Umetsu (*Biochem. Z.*, 1923, **135**, 442—479).—With a specially designed apparatus, the author has examined the electroendosmotic behaviour of solutions through a carbon filter. Blood charcoal has an isoelectric point at p_H 3 and in general in acid solution is positively charged through adsorption of hydrogen-ions, but is negatively charged in alkaline solution through adsorption of hydroxyl-ions. Sulphosalicylic acid is a strong dibasic acid, but it is unexpectedly found that the anion is more strongly adsorbed than the hydrogen-ion by blood charcoal. A substance like charcoal which functions as an ampholyte but is not molecular disperse is termed an "ampholytoid." Unlike blood charcoal, sugar or benzoic acid charcoals are positively charged over the whole range examined and adsorb basic dyes well, blood charcoal adsorbing acid and basic dyes. This only applies to adsorption of ions, indifferent surface-active substances like octyl alcohol being adsorbed equally by all varieties of charcoal examined.

H. K.

Solubility Relations in Mixtures containing Polar Components. F. Spencer Mortimer (*J. Amer. Chem. Soc.*, 1923, **45**, 633—641).—In an earlier paper, the author described a graphical method for calculating the ratio of the experimental to the ideal slope of the curves obtained by plotting the logarithm of the molecular fraction of dissolved substance against the reciprocal of the absolute temperature of the solubility point of the mixture and, hence, for calculating the solubility in non-ideal solutions (A., 1922, ii, 621). In the present paper, the author shows to what extent the generalisations previously discussed may be applied to such systems. Tables of solubilities of fluorene, *p*-dibromobenzene, benzoic acid, resorcinol, acetamide, and acetanilide in ethylene dichloride, chlorobenzene, nitrobenzene, *p*-xylene, toluene, benzene, pyridine, carbon tetrachloride, aniline, acetone, acetic acid, ethyl and methyl alcohols, phenol, acetophenone, urethane, and *p*-toluidine at various temperatures are given, many of which represent the results of new determinations. The ideal solubility of the solute has been calculated in every case. It is shown that the deviations from Raoult's ideal solubility law are

proportional to the magnitude of the differences of the internal pressures of the components of the system. The ratio of the experimental slope of the curve of log N against $1/T$ to the ideal slope, calculated from the latent heat of fusion, for any solute, is a measure of the relative internal pressures of the solute and the solvent. Not only may the latent heat of fusion of solids be determined, but relative values for the internal pressures of many solids and liquids may be calculated from solubility data by the application of the principles developed. The results of the calculations of relative internal pressures have been given and compared with those obtained by direct measurement or by other methods of calculation. A table of the relative internal pressures of sixty-eight substances referred to naphthalene as unity calculated from solubility data is included in the paper. The principles entering into the procedure for calculating solubilities of organic compounds in various solvents have been discussed both for polar and non-polar substances, and the limitations of the method pointed out. J. F. S.

A Survey of Existing Crystal Structure Data. RALPH G. WYCKOFF (*J. Franklin Inst.*, 1923, **195**, 182—210, 349—365, 531—549).—A critical summary of work published on X-ray diffraction effects made for the direct study of atomic arrangements.

Rhythmic Crystallisation. HANS KÄGI (*Helv. Chim. Acta*, 1923, **6**, 264—266).—By crystallisation from a mixture of alcohol and glacial acetic acid or from benzene of *r*-menthyl benzylacetate, concentric crystalline rings are obtained, showing extremely well the phenomenon of rythmic crystallisation. As crystallisation proceeds at the rate of about 1 cm. per minute, the phenomenon can be followed readily under the microscope. A number of photographs are reproduced. The *l*-ester does not crystallise in this manner. E. H. R.

The Recrystallisation of Metals and Salts. G. TAMMANN and Q. A. MANSURI (*Z. anorg. Chem.*, 1923, **126**, 119—128).—In a mass of metal some of the crystals grow at the expense of others, these crystallites being already in contact. In the case of powders the investigation is more difficult. Metallic powders are covered by a thin film of oxide, and when the powder is stirred these films are destroyed. When two particles having the same lattice structure touch they join; if, however, the lattice structure is different, then movement of atoms is necessary before union can take place. A stirrer was slowly rotated in the metallic powder and the temperature gradually increased. In the case of metals, the stirrer suddenly stopped at temperatures between 120° and 140°, this temperature being independent of the melting point of the metal. In the case of salts, the rate of stirring gradually decreased and finally stopped, this temperature being dependent on the melting point of the salt. These temperatures denote the temperature at which there is motion of the atoms in the solids. W. T.

The Mutual Increase and Decrease in Size of Metallic Crystallites which are in Contact in a Conglomerate. RUDOLF VOGEL (*Z. anorg. Chem.*, 1923, **126**, 1—38).—The crystallite conglomerate of a metal is not generally stable, because when the temperature is sufficiently high the frontiers between the crystallites change and a crystal which is itself invaded by one crystal may at the same time grow at the expense of another. This movement does not necessarily mean an increase in the size of the crystallites. Of two crystallites in contact, the one with the more stable structure, *i.e.*, the one containing the denser grouping of atoms on its surface, will grow at the expense of the other. When all the unstable contacts have disappeared, then movement of frontiers ceases. W. T.

Stability of Suspensions of Solid Particles of Proteins and Protective Action of Colloids. JACQUES LOEB (*J. Gen. Physiol.*, 1923, **5**, 479—504).—The stability of a suspension of gelatin-coated collodion particles is minimal at the isoelectric point of gelatin, and at this point it is increased by the addition of small quantities of salt. Gelatin itself is least soluble at the isoelectric point, and its solubility is increased by salts. This is not due to the charge conferred on the gelatin particles by the salt, as cataphoretic experiments show that at the isoelectric point gelatin-coated collodion particles are practically as completely uncharged in the presence of salt as they are before salt is added, but it would appear that such effects are due to the increase in the real solubility of isoelectric gelatin on the addition of salts. This is borne out by the fact that approximately identical concentrations of salts are required to precipitate gelatin from solution, and to flocculate such suspensions. If, on the other hand, the collodion particles be coated with genuine egg-albumin, the stability of the suspension depends primarly on the potential difference between the particle and the surrounding liquid, and instability occurs as soon as the potential falls below 10—13 millivolts, a critical potential agreeing with that of particles of denatured egg-albumin. It is concluded that egg-albumin is denatured when it forms a film round a solid particle. Results similar to those obtained with egg-albumin are obtained with casein and with edestin.

These facts are discussed in the light of Langmuir's theory of the affinity of certain groups for water. The high protective power of gelatin depends on the greater affinity for water of the molecule of this substance, in other words, on the high true solubility of gelatin. W. O. K.

Action of Trypsin on Colloids and the Influence of Neutral Salts on this Action. E. STIASNY and W. ACKERMANN (*Koll. Chem. Beihefte*, 1923, **17**, 219—255).—The action of trypsin on colloids depends on the previous history of the colloid, and in particular on the extent to which swelling has taken place. This fact probably explains the contradictory results obtained on the action of trypsin on colloids. A number of experiments on the action of neutral salts on the trypsin action have been carried out, chiefly with powdered hide. This substance has been used because

comparable results are more easily obtained than with pieces of hide and the experimental conditions can be kept nearer those obtaining in the tanning process. In all experiments, the hydrogen-ion concentration has been measured and taken into account in the subsequent discussion. In comparative swelling experiments, the swelling height of the hide powder has been measured in long tubes. Potassium thiocyanate, iodide, nitrate, and chloride show a moderate swelling action when present in $N/100$- or $N/10$-solutions, a sharp maximum in N-solutions, and a definite retarding effect in concentrated ($3N$—$5N$) solutions. In the case of potassium sulphate the maximum swelling is with $N/10$ solution. At 37°, the swelling is always greater than at 20°. When arranged according to the height of the swollen material, the anions of the salts investigated fall into the Hofmeister series. That this regularity should occur at the same P_H value in the solutions investigated, is evidence against the views of Loeb, which questions the correctness of the Hofmeister series. The swelling in the present case is accompanied by a partial peptisation, which is greatest with most strongly swelling solutions of salts. When this peptisation is taken into account, the difference in the swelling action of the various salts is more strongly marked. Trypsin in the presence of neutral salts has been allowed to act on hide powder at 37° and 20°, and the proteolytic and peptolytic action measured after two hours, twenty-four hours, and six days. This has been carried out by observing the swelling height and the formol titration value, and by examining the filtrate from the hide powder for its content of tanning material and total nitrogen. Numerous experiments with potassium thiocyanate of various concentrations show that $N/100$- and $N/10$-solutions of this substance have no action on either the proteolytic or peptolytic action of trypsin, N-solutions increase the proteolytic action of pancreas tryptase strongly, but retard the action of pancreas peptase, and $5N$-solutions completely stop both actions of trypsin. This shows that potassium thiocyanate influences the proteolytic trypsin action in exactly the same way as the swelling action. Increase of the trypsin concentration and the temperature accelerate the trypsin action without changing the regularity between the swelling and proteolytic trypsin action. Similar experiments have been carried out with potassium iodide, chlorate, nitrate, chloride, and sulphate, and the influence of various salt concentrations on the trypsin action investigated. The results show that the action of the salt on the substrate and that on the ferment must be differentiated. With strongly swelling salts and for the concentrations which most strongly promote the swelling, the action on the substrate is most noticeable and the swelling action and proteolytic action of the trypsin run parallel. In many cases, such as those of potassium nitrate and potassium chloride, the action of the salt in high concentrations appears to be overwhelmingly on the ferment; $4N$-solutions of these salts retard the swelling, but have no retarding action on the proteolytic trypsin action which up to concentration of N has not shown a maximum. In the peptolytic trypsin action, the influence of the neutral salts is restricted to the ferment. The

independence of the peptolytic and the proteolytic actions is particularly marked with N-potassium thiocyanate and N-potassium iodide, which promote strongly the proteolytic trypsin action but retard the peptolytic action. Hide powder is much more sensitive to trypsin than pieces of hide, probably because in the powder the outer layer is so changed in the preparation that it is more easily peptised. J. F. S.

Statistical Theory of Unimolecular Reactions. W. H. RODEBUSH (*J. Amer. Chem. Soc.*, 1923, **45**, 606—613).—A theoretical paper in which a statistical theory of unimolecular reactions has been developed. An equation has been derived from the kinetic theory for the rate of reaction of a unimolecular reaction. This equation has the form $\overline{N} = N\sqrt{RT/E_0\pi} \, . \, e^{-E_0/RT}$, where $\overline{N}$ is the number of molecules which possess vibrational energy is excess of the critical amount, and the other terms have their usual significance. In the two cases where data are available, namely, the vaporisation of mercury (Menzies, A., 1920, ii, 11) and Daniels and Johnston's experimental results on the decomposition of nitrogen pentoxide (A., 1921, ii, 249), the equation gives results which are probably as accurate as the data themselves. J. F. S.

Decomposition of Nitrogen Pentoxide. M. BODENSTEIN (*Z. physikal. Chem.*, 1923, **104**, 51—54).—A discussion of a paper by Daniels and Johnston (A., 1921, ii, 249) on the decomposition of nitrogen pentoxide. The author points out that two values in the published results give constants not in keeping with the other measurements. These are shown to be due to the particular temperature at which the experiments were carried out. It follows therefore that the thermal decomposition of nitrogen pentoxide is a purely unimolecular reaction, $N_2O_5 \rightarrow N_2O_3 + O_2$, and constitutes the first case of the exact examination of a unimolecular gas reaction. The constants obtained by Daniels and Johnston are therefore to be multiplied by 5/6. J. F. S.

Kinetic Interpretation of the Law of Van't Hoff. C. E. GUYE (*Compt. rend.*, 1923, **176**, 835—836).—It has already been shown that on the supposition that a dissociating action is a function of the impulse of the forces developed during collisions, the number of parietal collisions causing dissociation per unit of surface in unit time is given by the relation $\nu_0 = [n/2\sqrt{hm\pi}]e^{-hmv_0^2}$, and the number of collisions between molecules by the expression $\nu_0' = [n^2\sigma^2\sqrt{2\pi/hm}]e^{-2hmv_0^2}$ (*Arch. Sci. phys. nat.*, 1922, 132—153), the factors between brackets representing, respectively, the total number of collisions, and the exponentials the fractions of these numbers which are followed by dissociation. It is shown that this hypothesis accounts quantitatively for the approximate rule of van't Hoff, according to which at the ordinary temperature an elevation of temperature of 10° doubles the velocity of a reaction, and a numerical verification is given for the case of hydrogen, which can be extended to any gas, for in order to obtain the velocities of dissociation comprised between the same experimental limits,

it is only necessary to choose ν_0 inversely proportional to the square root of the molecular weight, and the exponential, on which the velocity of dissociation mainly depends, retains then the same value.

G. F. M.

Halogenate Reductions. The Reduction of Iodate and Chlorate by Arsenious Acid. HANS KUBINA (*Monatsh.*, 1923, **43**, 439—468).—The reduction of chlorate and iodate by arsenious acid has been investigated, and these two processes have been shown to be examples of coupled reactions. The reaction velocity is independent of the concentration of arsenious acid. The actual reaction measured is the slow reduction of halogenate by halide, this reaction being followed by the rapid oxidation of arsenite: $XO_3'+X' \rightarrow A$ (measurable); $A+As^{III} \rightarrow X'+As^{V}$ (rapid), where A is an intermediate compound.

The oxidation of arsenite by iodic acid proceeds with rapid initial acceleration, owing to the catalytic effect of the iodidion produced.

The reaction mechanism of chlorate reduction is probably: (*a*) Measurable reaction: $ClO_3'+Cl'+2H^{\cdot} \rightarrow H_2ClO_3+Cl$, followed by the rapid reactions, (*b*) $H_2ClO_3+4Cl'+4H^{\cdot} \rightarrow 5Cl+3H_2O$, and $3Cl_2+3AsO_3'''+3H_2O \rightarrow 3AsO_4'''+6Cl'+6H^{\cdot}$. The initial velocity of interaction of chloric acid and arsenite does not increase rapidly; catalytic acceleration by chloridion is not observed, owing to the high initial concentration of this ion. Were the latter present, initially, in small quantities, such catalytic accelerative influence should be in evidence. On this supposition, the velocity of chlorate reduction by arsenite would be expressed by the equation: $dx/dt=[K_1+K_2(S)^x(Cl')](ClO_3')$.

In iodate reduction the mechanism is probably: (*a*) Measurable reaction: $IO_3'+2I'+H^{\cdot} \rightarrow HIO+2IO'$, followed by the rapid reactions (*b*) $2IO+2AsO_3''' \rightarrow 2AsO_4'''+2I'$, and $HIO+AsO_3''' \rightarrow AsO_4'''+H^{\cdot}+I'$, giving the velocity equation: $dx/dt=[K_1+K_2(I')_2](IO_3')(H^{\cdot})$.

Schilov's work (A., 1903, ii, 276) on bromate reduction is also discussed. See also Bray (A., 1906, ii, 223) and Luther and McDougall (A., 1908, ii, 361).

E. E. T.

Rate of Reaction between Ethylene and Bromine. T. D. STEWART and K. R. EDLUND (*J. Amer. Chem. Soc.*, 1923, **45**, 1014—1024).—If the apparently bimolecular additive reaction between ethylene and bromine is preceded by a dissociation or opening of the double bond of the ethylene with formation of tautomerides (Nef., A., 1905, i, 109), a purely bimolecular reaction may still be anticipated if the rate of tautomerism is rapid compared with the addition of bromine; this is true whether only one or all of the tautomerides can react. Positive conclusions respecting tautomerism can, therefore, be drawn only if a deviation from the bimolecular reaction is observed.

Such a deviation is found only to occur during the first twelve seconds after mixing the reagents, and is ascribed to surface catalysis;

the subsequent reaction is strictly bimolecular. The assumption of tautomeric forms of ethylene is therefore unnecessary.

Two air streams, containing known amounts of ethylene and of bromine, respectively, are completely mixed at 0°, in less than one second, in the apparatus described. The mixed gases are passed into a bulb to which a manometer is attached. A side tube allows the gas to be sampled immediately before it enters the reaction bulb. After sampling, the bulb is closed and the reaction followed by observing the decrease in pressure. The measured sample is analysed for bromine by absorbing the latter by means of potassium iodide solution and titrating the liberated iodine; the gas issuing from the sampler is collected and estimated for ethylene. The volume of the reaction bulb is varied in different experiments.

The reaction takes place for the most part, if not entirely, on the walls of the containing vessel; no gaseous reaction is detected. The reaction is promoted by the presence of moisture. With a constant surface, the rate of the reaction is proportional to both the concentration of ethylene and the concentration of bromine.

W. S. N.

Velocity of Hydrolysis of Acetic Anhydride. ANTON SKRABAL (*Monatsh.*, 1923, **43**, 493—506).—The hydrion produced in the reaction: $Ac_2O+H_2O=2AcOH$ is measured by its effect on the velocity of the interaction of iodide and iodate (cf. A., 1918, ii, 12, and Dushman, A., 1904, ii, 718). As solvent, aqueous acetone (containing 2·5 vols.% of the latter) is used. In order to obtain the end-point for total hydrolysis, it is necessary to use an excess of iodide–iodate mixture. With one minute as time unit and at 25°, the reaction velocity of hydrolysis of acetic anhydride is k_w 0·19. The same value was obtained in three different experiments in which the hydrion concentration varied considerably, and therefore is an accurate measure of the hydrolysis by water (*i.e.*, k_s is negligible). The constant for the alkaline hydrolysis occurring in the same experiments was calculated and found to be $k_a \leqq 4{\cdot}4\times10^6$, a figure not appreciably larger than that for esters which are readily hydrolysed by alkalis.

In presence of larger quantities of acetone, k_w is decreased, this effect being due to the medium effect in addition to the mere dilution effect.

It is shown, by considering the hydrolysis of various substances containing the group -CO·OR (where R is alkyl or acyl), that, in addition to catalytic hydrolysis by hydrion or hydroxyl-ion, a considerable amount of hydrolysis by water (undissociated) occurs, if hydrolysis is not appreciably reversible.

E. E. T.

Hydrolysis of the Lactide from Lactic Acid. OTTO RINGER and ANTON SKRABAL (*Monatsh.*, 1923, **43**, 507—523).—A continuation of work by Johansson and others (A., 1918, ii, 223; 1922, i, 425).—The velocity of the two-stage hydrolysis of lactide has been measured in aqueous acetone solution (2·5 vol.% of acetone) at 25°. For the first stage (lactide to lactyl-lactic acid), alkaline, acid, and water hydrolyses give k_{1a} $1{\cdot}2\times10^6$, k_{1s} 0·1088 and k_{1w} 0·00459. For

the second stage (lactyl-lactic acid to lactic acid), the values k_{25} 19·5 and k_{25} 0·00203 were obtained. The alkaline hydrolysis in the first stage proceeds with a rapidity similar to that observed in the first stage of the hydrolysis of dimethyl oxalate (A., 1918, ii, 12). In fact, lactide and the normal oxalic esters may be titrated as if they are free monobasic acids.

Acetone and alcohol decrease the velocity of the above hydrolysis. The dissociation constant of lactyl-lactic acid (determined by means of indicators) is $9·9 \times 10^{-4}$ at the ordinary temperature.

E. E. T.

Inversion of Lactose by Strong Acids. I. B. BLEYER and H. SCHMIDT (*Biochem. Z.*, 1923, **135**, 546—557).—The velocity of inversion of lactose has been determined with hydrochloric acid (*d* 1·185), with perchloric acid (*d* 1·67), and with sulphuric acid (22 and 24*N*). The reaction is unimolecular, and from measurements at different temperatures the speed is shown to be quadrupled for a rise of 10°. The authors propose the formula $K=a\,.\,t^{b\,.\,t}$ for the relation between the temperature and the velocity constant. The velocity falls off with increasing content of lactose. H. K.

Inhibition Phenomena in Chemical Reactions (especially in the Solution of Metals in Acids). A. SIEVERTS and P. LUEG (*Z. anorg. Chem.*, 1923, **126**, 193—225).—An investigation of the effect of various poisons on the rate of solution of metals in acids, particularly of iron in hydrochloric and sulphuric acids and aluminium and zinc in hydrochloric acid. It was found that ferrous sulphate, methyl sulphate, ammonium chloride, tetramethylammonium chloride, choline hydrochloride, and taurine have no inhibiting effect. Potassium cyanide, caffeine, theobromine, coniine, pyramidone, pyridine, atropine, quinoline, *iso*quinoline, and codeine had a slight inhibiting effect. Nicotine, veratrine, cocaine, and cinchonine were more effective, whilst α- and β-naphthaquinolines, strychnine, brucine, narcotine, and quinine were very effective. The most effective inhibitant was an "extract" consisting of the ether-soluble basic constituents of crude anthracene. It was found that the amount of inhibition was much the same in both acids, but with theobromine, nicotine, cinchonine, narcotine, and quinine, the inhibiting effect was more marked in hydrochloric acid. The authors conclude that all compounds containing pyridine nitrogen are more or less effective inhibitants. Analogous results were obtained with aluminium and zinc.

It is found that the velocity of solution of iron in hydrochloric acid at 78° is approximately proportional to the cube of the concentration of the acid. The temperature coefficient of the solution velocity is 2·0—2·3 per 10° between 50° and 78°. For slight amounts of poisoning, increase of temperature reduces the inhibition: for larger amounts, it has no effect. In the case of aluminium, the solution velocity also has a large temperature coefficient (1·4 from 20—30°), but it is reduced to zero in the presence of large amounts of poison. The poisoning and de-poisoning of metals occurs very quickly.

An empirical formula is proposed: $(K_0-K_c)/K_c=ac^b$; where K_0 is the rate of solution with no poisoning, K_c is the rate of solution at poison concentration c, and a and b are constants depending on the nature of the poison. It is found to break down for inhibitions greater than 75—85%.

The influence of poisons on the overvoltage of metals was also investigated. α-Naphthaquinoline has little effect. "Extract" increases the overvoltage of nickel, iron, and copper, and, to a less extent, of mercury, silver, and lead: it has no effect on platinised platinum. No obvious connexion between the inhibition of solution in acid and the increase in overvoltage could be found, but it is considered that adsorption of the poison occurs on the metal surface, thus reducing the amount accessible to the acid. H. H.

The Solution Velocity of Copper in Dilute Benzaldehyde and its Dependence on the Viscosity. FRITZ SCHAAF (*Z. anorg. Chem.*, 1923, **126**, 237—253).—The experimental results of Bernoulli and Schaaf (A., 1922, i, 1029) are used, and an explanation of the form of the solution velocity-concentration curves is put forward. The solution velocity is a resultant of two effects, the concentration of benzaldehyde (that is, its active mass) and the fluidity of the solution, an increase in either factor increasing the velocity. An increase in the former factor, however, results in a decrease in the latter, so that the velocity-concentration curves rise to a maximum and subsequently fall to zero velocity at 100% concentration of benzaldehyde. At 50°, the maxima for benzene and toluene solutions occur at concentrations of 14 and 16%, respectively, of benzaldehyde, the solution having a fluidity of 127 c.g.s. units in each case. No reaction takes place between copper and benzaldehyde in any solution with a fluidity of less than 60.

It is found that the rate of solution is practically unaffected by stirring, and that in the tranquil state the rate of solution in the heterogeneous system depends on the temperature in the same way as does the velocity of a reaction in a homogeneous system. The temperature coefficient, however, is smaller in the former case. H. H.

Catalytic Actions at Solid Surfaces. X. The Interaction of Carbon Monoxide and Hydrogen as Conditioned by Nickel at Relatively Low Temperatures. A Practical Synthesis of Methane. E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1923, [*A*], **103**, 25—34; cf. A., 1922, ii, 757).—Certain known interactions of carbon monoxide and hydrogen or steam in the presence of metallic catalysts are briefly reviewed, and attention is directed more especially to the behaviour of purified water-gas in the presence of various finely divided metals, other than copper, at temperatures between 200° and 300°. It is shown that, under these conditions, a new type of reaction represented by $2CO+2H_2=CO_2+CH_4$ occurs, which, although never complete, proceeds to a very considerable extent. The mechanism of the action is briefly discussed, and it is suggested that in the presence of water vapour, considering two molecular volumes of water-gas, the following

reactions occur: $CO+H_2O=CO_2+H_2$; $CO_2+2H_2+H_2=CH_4+H_2O$. Nickel is the most efficient catalyst in this connexion. With cobalt, the reaction commences at a somewhat lower temperature, about 180°, and is subsidiary to the reactions $CO+3H_2=CH_4+H_2O$; $2CO=C+CO_2$. Silver is inert, iron almost so, and platinum and palladium are of minor importance. Mixed catalysts, *e.g.*, copper-nickel, iron-nickel, cobalt-nickel, cobalt-platinum, and cobalt-palladium are less efficient than the corresponding single (cobalt or nickel) catalyst. At increased pressures up to 6 atmospheres, the process proceeds much as at atmospheric pressure, except that, in the case of nickel, the minimum temperature of interaction rises with increasing pressure. As by this reaction more methane is formed from water-gas than by other methods, the proportion of methane being 25% of the water-gas decomposed compared with a maximum of 20% by other reactions, it is suggested that the process may find application in increasing the methane content of town gas, or in the manufacture of pure methane. In technical practice, repeated passage of purified water-gas over nickel at 240—270° would remove all carbon monoxide. J. S. G. T.

Catalysis [of the Decomposition] of Hydrogen Peroxide by Colloidal [Basic] Ferric Salts. J. DUCLAUX (*J. Chim. Phys.*, 1923, **20**, 18—29).—The velocity of decomposition of hydrogen peroxide at 25° in the presence of colloidal solutions of ferric chloride has been investigated. The colloidal solutions were prepared by boiling solutions of ferric chloride and dialysing the sol thus obtained. The decomposition is shown to take place according to equations for a reaction of the first order. In solutions of the same acidity and containing a given hydrosol, the velocity constant is proportional to the concentration of the iron. The reaction is not due to the whole micella, but takes place through the active and ionisable portion of the micellae. The ferric-ion from a colloidal complex has the same activity as the ferric-ion from a molecule of ferric chloride. The demands of the electrochemical micellar theory put forward previously by the author (A., 1910, ii, 108) are shown to be fulfilled both qualitatively and quantitatively in the present experiments. The general theory of the action of diastase has been considered from the point of view of this theory, and it is shown that the action of ions in the diastatic change appears to be fundamental. The poisoning of diastase is probably due to ordinary chemical processes between the active ions or the diastase-ions.

J. F. S.

Auto-oxidation and Antioxygen Action. Catalytic Properties of Iodine and its Compounds. The Case of Acraldehyde. CHARLES MOUREU and CHARLES DUFRAISSE (*Compt. rend.*, 1923, **176**, 797—803).—The action of iodine as an antioxygen both free and in organic and inorganic combination was studied as regards its behaviour in the auto-oxidation of acraldehyde. Metallic iodides with the exception of those of mercury and silver, and the hydriodides of organic bases behaved distinctly as antioxygens in concentrations of 1 in 1000 or less, their power in this respect being of the same

order as that of the phenols. Thus methylamine hydriodide in a concentration of 1 in 1,000,000 showed a distinct retarding action on the oxidation, whilst 1 in 1,000 prevented oxidation for at least a month, differing in this way from the action of the phenols, which did not cause a complete cessation of oxidation, but rather a retardation of the velocity. With the iodides, on the contrary, the first phase, at all concentrations, was characterised by a complete cessation of oxidation for a certain period, followed by a second period in which the oxidation suddenly commences with a velocity equal to, or even exceeding, that of pure acraldehyde. This positive catalysis, however, was infinitely less intense than the original negative catalysis. In the case of the organic iodine compounds, such as methyl iodide, iodoform, allyl iodide, iodosobenzene, etc., although their action is the same in principle, the period of negative catalysis is greatly abbreviated, and in general greater concentrations are required to produce any observable effect. Thus the period of negative catalysis or antioxygen action with methyl iodide 1 in 80 lasted only a few seconds, with methylene iodide 1 in 100, fifteen minutes, with iodoform 1 in 100, twenty hours, benzyl iodide 1 in 1000, seventy hours, etc. The retarding action of free iodine at 1 in 1000, lasts for several hours. The iodine-ion appears from these results to be the most energetic negative catalyser, and the transition to positive catalysis must be attributed to a change in the catalyst. The bearing of the results on the biological action of iodine compounds is discussed. G. F. M.

Reactions of Formic Acid at the Surface of Alumina. Selective Activation of Alumina. II. HOMER ADKINS and BRYNJULV H. NISSEN (*J. Amer. Chem. Soc.*, 1923, **45**, 809—815).—Data are presented to show that by modifying the distance between the aluminium atoms, alumina may be selectively activated towards the following reactions: (1) $H\cdot CO_2H = CO_2 + H_2$; (2) $H\cdot CO_2H = CO + H_2O$.

The experimental method is similar to that previously employed (Adkins, A., 1922, ii, 834); the following catalysts are used: (1) alumina from the action of water on aluminium amalgam, (2) alumina from aluminium *iso*propoxide on pumice, (3) alumina from aluminium *iso*propoxide in pills, (4) alumina from aluminium butoxide on pumice, (5) glass wool, and (6) pumice. For each catalyst a curve is constructed showing the relation between the temperature of reaction and the ratio (formic acid equivalent to CO)/(formic acid equivalent to CO_2). For the first and second catalysts this ratio is also plotted against the concentration of acid in the vapour phase.

From the first set of curves, it is evident that the velocity constants of the reactions (1) and (2) are not only differently affected by the same catalyst, but that different catalysts show different selective catalysing power. The second pair of curves show clearly that the presence of water alters the ratio of the two velocity constants (cf. Hinshelwood, Hartley, and Topley, A., 1922, ii, 274).

It is claimed that these results do not accord with the hypothesis of selective adsorption as to the mechanism of catalysed reactions,

but are more readily explained in terms of an extension of Langmuir's theory of the mechanism of reactions at surfaces. W. S. N.

Platinum Oxide as a Catalyst in the Reduction of Organic Compounds. II. Reduction of Aldehydes. Activation of the Catalyst by the Salts of certain Metals. WALLACE H. CAROTHERS and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1923, **45**, 1071—1086).—Platinum black from platinum oxide prepared from absolutely pure chloroplatinic acid becomes very quickly inactive when shaken with an aldehyde in an atmosphere of hydrogen; only by frequent reactivation can the reduction be completed. The addition of as little as 4 parts per million of iron as ferrous or ferric chloride greatly accelerates the reduction. A systematic study of the effect of various amounts of ferrous and ferric chloride on the catalytic reduction of benzaldehyde, and of ferrous chloride on that of heptaldehyde, using the platinum oxide catalyst previously described (A., 1922, ii, 558) shows that an optimum effect is produced when an amount of iron chloride corresponding with about 0·0001 mol. in 100 c.c. is used. Larger concentrations of ferrous chloride only slightly diminish the rate of reduction, besides causing a tendency for the reduction to proceed beyond the alcohol stage. When ferric chloride is used, it is first reduced to ferrous chloride; with amounts exceeding 0·001 mol. per 100 c.c., an induction period appears, and the reduction is retarded because of the hydrogen chloride set free in the reduction of the ferric chloride. Moreover, the reduction proceeds beyond the formation of benzyl alcohol to toluene and even further. It is shown that impurities sufficient to increase the activity of the catalyst invariably appear during its recovery.

Evidence is given for the following interpretation of the effect of the ferrous salt. The inactivity of the pure platinum black is due to the fact that it is deprived of the oxygen necessary for its activity by the readily oxidisable aldehyde. The iron salt specifically inhibits this reaction and so prolongs the active life of the catalyst.

Using appropriate amounts of ferrous chloride and 0·23 g. of catalyst, it is shown that 21·2 g. of benzaldehyde may be smoothly reduced to the alcohol in twenty to twenty-five minutes. The reaction then stops and no further reduction occurs. A method is described for reducing 100 g. of benzaldehyde in four hours with 0·025 g. of catalyst. W. S. N.

The Dynamo-kinetic Theory of the Electron and the Atom. TH. TOMMASINA (*Compt. rend.*, 1923, **176**, 892—894).—A theoretical paper in which the author develops the conception of indivisible and indestructible units of energy termed *energons* as the ultimate constituents of the electron. As the movement of the energon is indestructible, its dynamo-kinetic value is invariable. The energon is to be regarded as being at the same time the indivisible quantum of energy, and the indivisible unit of matter. Its rotative velocity is the greatest that can exist and its energy being a function of its

velocity it combines in itself the maximum of energy with the minimum of matter.. G. F. M.

Whittaker's Quantum Mechanism in the Atom. H. A. LORENTZ (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **25**, 414—422). —A theoretical paper in which, on the basis of Whittaker's quantum mechanism of the atom (A., 1922, ii, 632), the author evolves relationships to express the action between an electron and an atom during a collision. The author also attempts to generalise the ideas of Whittaker. J. F. S.

Chemical Combination and Ewing's Magnetic Atom. A. P. LAURIE (*Proc. Roy. Soc. Edin.*, 1922, **42**, 352—361).—In order to bring the Ewing magnetic atom (cf. A., 1922, ii, 632) into line with the ordinary conception of a chemical atom, it is assumed that the inner electrons form a fixed system of magnets with the *N*-poles pointing inwards, and that the outer electrons form a rotating unit around the first. Each of the outer electrons is capable of rotation about a central pivot. During chemical combination, the outer electrons oscillate about their centres, and fall into new positions with the conversion of work into heat. The mechanism of ionisation and catalysis is discussed from this point of view. A model is given in which eight electrons are arranged in a ring, so as to exert no external magnetic polarity, with an additional electron in an outer shell. The atoms in a chemical compound are considered to be held together by means of the outer electrons by the electrostatic and magnetic attractions brought into play. A Langmuir atom is constructed, in which eight ring electrons are arranged radially around a central nucleus, and a single electron in the outer shell is placed so that the lines of force passing through it are at a maximum. In chemical combination, the valency electrons swing through 90° to take up a new position under their mutual polar attractions. According to the arrangement of the ring electrons in the nucleus, combination may take place with or without ionisation. A simple explanation is given of the production of an electric current during a chemical reaction without local production of heat. W. E. G.

The Hypothesis of Constant Atomic Radii. RALPH W. G. WYCKOFF (*Proc. Nat. Acad. Sci.*, 1923, **9**, 33—38).—Calculations of the spheres of influence of atoms can be made from four independent starting points: (1) from metals, (2) through the diamond and the bivalent metal carbonates of the calcite group, (3) from pyrites (FeS_2), (4) from cæsium dichloro-iodide ($CsCl_2I$). Atomic radii determined by these different methods of approach do not agree among themselves. The results from pyrites, and cæsium dichloro-iodide are fairly concordant, however, and these have been employed in testing the hypothesis of constant radii (W. L. Bragg, A., 1920, ii, 537). The available data are grouped into two tables, in one the concordant results, and, in the other, those measurements in opposition to the hypothesis being given. The rule is obeyed only in those cases where the atomic environment is practically identical. Thus, the hypothesis is true in large groups of isomorphous

compounds, consisting of two kinds of atoms, like the alkali halides which have the sodium chloride arrangement. On the other hand, radical differences in atomic environment lead to marked changes in the interatomic distances. W. E. G.

Twenty-ninth Annual Report of the Committee on Atomic Weights. GREGORY PAUL BAXTER (*J. Amer. Chem. Soc.*, 1923, **45**, 563—572).—An account of the determinations of atomic weights published during 1922. The report includes new work on carbon, hydrogen, glucinum, boron, nitrogen, oxygen, sodium, chlorine, selenium, bromine, yttrium, silver, antimony, lanthanum, thallium, lead, and mercury, together with the references to the literature.
J. F. S.

Quantum Theory of Polyatomic Molecules. M. BORN and E. HÜCKEL (*Physikal. Z.*, 1923, **24**, 1—12).—The method of quantisation of disturbed systems developed by Born and others (*Z. Physik*, 1921, **6**, 140; 1922, **8**, 205; **10**, 137) is applied to deduce the theory of the mutual interdependence of degrees of freedom of rotation and vibration proposed by Kratzer (A., 1921, ii, 140, 142) to explain the band spectra of diatomic molecules. On the assumption that the potential energy of a system of atoms depends only on the distances between nuclei, a mathematical theory applicable to the spectra of diatomic and polyatomic molecules is developed. In the case of diatomic molecules, and of triatomic molecules having atoms arranged in a straight line, the axis of rotation remains stationary in space. In general, with polyatomic molecules, the axis of rotation is not stationary. The theory is applied in detail to the case where the molecules in equilibrium are arranged over the surface of a symmetrical top. J. S. G. T.

Two New Micro-methods for the Determination of Molecular Weights. K. RAST (*Z. physiol. Chem.*, 1923, **126**, 100—119).—The first method is a modification of Barger's micro-method (T., 1904, **85**, 286). The modification consists in the fact that one single drop occupying two or three cm. of the capillary, of each of the two solutions that are to be compared—standard and unknown—is used. One of these drops is fixed at one end by being attached to the closed end of the capillary, and the other end of this fixed drop is observed at intervals, and changes in its position are noted. No change takes place if the solutions are isotonic. Full details are given of the method of filling the capillary tubes.

The second method makes use of the high depression of the freezing point obtained when camphor is used as a solvent. By the use of micro-apparatus and of small quantities of the solvent, determinations may be carried out with about 10 mg. of material.
W. O. K.

Electrovalency. I. The Polarity of Double Bonds. THOMAS MARTIN LOWRY (T., 1923, **123**, 822—831).

Co-ordination Compounds and the Bohr Atom. NEVIL VINCENT SIDGWICK (T., 1923, **123**, 725—730).

Some Factors Influencing Co-ordination. T. Martin Lowry (*Chemistry and Industry*, 1923, **42**, 316—319).—Co-ordination is the result of an attraction between ions which is similar, both in origin and in its geometrical effects, to the forces which bind together the ions in crystals, such as rock-salt. In the compounds of $\overset{++}{Fe}$, $\overset{+++}{Co}$, $\overset{+++}{Rh}$, $\overset{+++}{Ir}$, $\overset{++++}{Pd}$, and $\overset{++++}{Pt}$, six co-ordinated groups are just sufficient in number to complete the outer shell of electrons of the metal if each group shares one pair of electrons with the metal. The ammines, such as $[Ir(NH_3)_6]Cl_3$ and $[Pt(NH_3)_6]Cl_4$, and the metallic carbonyls, such as $Mo(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$, appear to owe their formation and stability to this sharing of electrons. Whilst a deficiency of one, two, or three electrons can be tolerated readily, the surplus electron of potassium cobalticyanide is expelled with great violence from the co-ordinated complex, giving rise to the extremely stable cobalticyanide.

Co-ordination usually involves the attachment to a metal of more radicles than it can carry according to the old theory of valency. The theory of "mixed double bonds" allows this to be expressed by means of symmetrical formulæ in compounds such as ferric acetate.

Tautomeric ions, which can be written in two ways since they possess two possible points of attachment for a hydrogen nucleus or an alkyl group, often give co-ordinated complexes in which multivalent ion is attracted to both points simultaneously. H. W.

Constitution of Hydrates. I. Hydrates of Salt-like Compounds. Max E. Lembert (*Z. physikal. Chem.*, 1923, **104**, 101—146).—A theoretical paper in which, on the basis of a simple geometrical conception of co-ordination linking, such as that of Werner and Kossel, steric numbers have been deduced which determine the possible co-ordination numbers for similar groups when added to a central atom. These steric numbers allow the drawing up of a system of the solid "whole number" hydrates of salt-like compounds, whereby the water molecules are arranged apart from the anion and kation. The mutual influence of the ions in hydrate formation is discussed in the light of Fajan's hypothesis, and this is confirmed. The system has been drawn up in special cases for the chlorides, sulphates, nitrates, and hydroxides of metals, and shown to be in keeping with facts. The lowest and highest hydrates in these groups can, with very few exceptions, be fitted into the system, and in the case of most of the exceptions, by means of a higher co-ordination number, which is shown to be likely, these can also be brought into the system. J. F. S.

Electrostatic Theory of Abnormal Liquids. Jakob J. Bikerman (*Z. physikal. Chem.*, 1923, **104**, 55—73).—A theoretical paper in which it is shown that when it is assumed that the molecular weights of the alcohols are normal, then the rules of Eötvos and van der Waals show that they have a slightly abnormal surface tension and vapour pressure. Both these abnormalities can be

explained by the assumption of the existence of an electric double layer on the surface of the alcohols. On the basis of this assumption, the thickness of the double layer is shown to be of ordinary molecular dimensions, and the potential spring has the same value as the electro-osmotically determined potential difference. The connexion of the anomaly with the power of the liquid to charge itself on contact with a foreign substance may be followed quantitatively. The connexion between the anomaly and the di-polar character is pointed out and the rôle of the partition of the dipoles in the establishment of the double layer is discussed. Since the Pictet-Trouton constant is unquestionably determined from the vapour-pressure formulæ, its unusual value in the case of the alcohols is explained by the present hypothesis. The abnormal viscosity and critical coefficients indicate the presence of large internal pressures which on calculation are found to have rational values. J. F. S.

The Dschâbir of the Eighth, and the so-called Geber (Pseudo-Geber) of the Thirteenth Century. EDMUND O. VON LIPPMANN (*Chem. Ztg.*, 1923, **47**, 321; cf. Holmyard, this vol., ii, 148; Partington, *ibid.*).—In reply to Partington's criticism (*loc. cit.*), the author maintains that his disbelief in the authenticity of the Latin works ascribed to Geber, and of Avicenna's "De Anima" is well founded. A. A. E.

Glass to Metal Joint. MERLE L. DUNDON (*J. Amer. Chem. Soc.*, 1923, **45**, 716—717).—A satisfactory glass-to-metal joint which is free from strain and capable of preserving high vacua may be made as follows. The glass tube is drawn out so that it fits easily for about 1 cm. into the copper tube. It is then coated with platinum and copper-plated over a length of 3—4 cm. by the usual electrolytic method. The coppered end is then polished until it fits tightly in the copper tube. Then copper is electrolytically deposited over the copper tube, joint, and a short length of the glass tube, so that an air-tight copper sleeve is formed which is free from strain and strong. J. F. S.

Inorganic Chemistry.

Apparatus for Electrolytic Preparation of Pure Hydrogen. GERHARD NIESE (*Physikal. Z.*, 1923, **24**, 12—14).—An apparatus for preparing pure hydrogen by the electrolysis of a 30% solution of chemically pure sodium hydroxide employing pure nickel electrodes is described. A cylindrical anode surrounds a similar shaped cathode, and diffusion of oxygen from the former to the latter is prevented by the use of an auxiliary nickel cathode, having the form of a truncated cone. J. S. G. T.

Hydrogen Hexasulphide and the Solubility of Sulphur in the Persulphides of Hydrogen. JAMES H. WALTON and EARL L. WHITFORD (*J. Amer. Chem. Soc.*, 1923, **45**, 601—606).—The solubility of sulphur in hydrogen disulphide and hydrogen trisulphide has been determined at temperatures from −34·72° to 55·3°. Both liquids dissolve large quantities of sulphur, the amount dissolved increasing very rapidly with increasing temperature up to −1·45° and above this temperature much less rapidly. The solubility curve shows a well defined break at −1·45°, and at this temperature the liquid has a composition very close to that required for hydrogen hexasulphide, H_2S_6. It is found that if either sulphide is saturated with sulphur at a given temperature, the two resulting liquid phases have the same composition. The hexasulphide is stable at temperatures below −1·45° and decomposes rapidly at higher temperatures.
J. F. S.

Solubility. VIII. Solubility Relations of certain Gases. NELSON W. TALOR and JOEL H. HILDEBRAND (*J. Amer. Chem. Soc.*, 1923, **45**, 682—694; cf. A., 1919, ii, 392; 1922, ii, 141).—The solubility of chlorine has been determined in heptane, carbon tetrachloride, silicon tetrachloride, and ethylene dibromide at various temperatures from 0° to 40°. The following values are recorded in g. per g. of solvent: heptane at 0°, 0·2036; silicon tetrachloride at 0°, 0·131; carbon tetrachloride 0°, 0·156, 19°, 0·0848, 40°, 0·0433; ethylene dibromide 20°, 0·0813, 40°, 0·0469. These data together with other data on the freezing-point depression in liquid chlorine, are discussed in the light of the theory of solubility previously put forward, and shown to be in accordance with the earlier predictions. Solubility data for hydrogen, nitrogen, carbon monoxide, oxygen, methane, carbon dioxide, nitrous oxide, chlorine, carbonyl chloride, niton, and actinium emanation are summarised and their theoretical relations discussed. J. F. S.

Behaviour of Ozone. E. H. RIESENFELD (*Z. Elektrochem.*, 1923, **29**, 119—121).—A *résumé* of the recent work on the preparation of pure ozone, its boiling point, critical constants, critical behaviour, and thermal equilibrium. J. F. S.

Sulphur Trioxide. A. BERTHOUD (*J. Chim. Phys.*, 1923, **20**, 77—86).—Several physical properties of sulphur trioxide have been investigated. The following values are recorded: m. p. 16·85°±0·02°; b. p. 43·84°/733·2 mm.; vapour pressure of the liquid 24°, 240·5 mm., 25°, 253·5; 27·8°, 302·0; 30·45°, 352·0; 34·8°, 454·0; 37·8°, 534·7; 41·4°, 643·7; 43·68°, 726·5; 45·6°, 796·3; 47·8°, 887·2; by interpolation from these figures, the boiling point at 760 mm. is 44·52°; critical pressure, 83·8 atms.; critical temperature, 218·3°; d^{20} 1·9255; d^{25} 1·9040; d^{30} 1·8819; d^{35} 1·8588; d^{40} 1·8335; d^{45} 1·8090; d^{50} 1·7812, and d^{55} 1·7752. The orthobaric density of liquid and gaseous sulphur trioxide has been determined nearly up to the critical point, and the critical density found to be 0·633. The surface tension measured by the capillary rise is found to be 19°, 34·17; 44·9°, 29·47, and 78·0°, 22·63. The association

constant calculated from these figures by the Eötvos method has the values 1·52 and 2·00, respectively. The van der Waals constants are calculated to $b=0·002684$ and $a=0·01629$. The observations made show that β-sulphur trioxide is not a simple polymeric modification of the α-variety, but probably an indefinite hydration compound. The law of rectilinear diameters could not be confirmed with sulphur trioxide. J. F. S.

The Halides of Tellurium. M. DAMIENS (*Ann. Chim.*, 1923, **19**, 44—119).—The author's work on tellurium iodide (A., 1921, ii, 110, 257, 399) and bromides (A., 1921, ii, 546, 636) is republished, together with similar work on the chlorides. The dichloride is only stable in the gaseous condition or in solution and in equilibrium with its decomposition products, tellurium and the tetrachloride. In the solid state, it dissociates into a solid solution of the element in the tetrachloride. In ethereal solution, it absorbs bromine and iodine, yielding substances which appear to be the chlorobromide and chloroiodide, respectively, but it was not found possible to isolate either of these. The dibromide, however, on addition of iodine under similar conditions, yields a bromoiodide which may be crystallised from the solution. The methods used in the work were those of thermal analysis in conjunction with the study of the composition of the vapour obtained from mixtures of known composition. H. J. E.

Determination of the Vapour Pressure of Metallic Arsenic. SHINKICHI HORIBA (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **25**, 387—394).—The vapour pressure of the grey modification of arsenic and its liquid have been determined over the temperature ranges 450—815° and 808—853°, respectively, by the same method as that used by Smits and Bohkorst (A., 1916, ii, 317) in the examination of phosphorus. The following values are recorded: solid, 450°, 0·026 atm.; 500°, 0·076; 550°, 0·222; 604°, 0·785; 615·5°, 0·997; 658°, 2·392; 697°, 4·85; 741°, 9·7; 772°, 16·9; 790°, 22·3, and 815°, 33·6; liquid, 808°, 34·2 atm.; 817°, 35·7; 830°, 38·1; 843°, 40·5; 850°, 41·6, and 853°, 42·2. Extrapolation of the vapour-pressure curves gives the melting point as 817—818° at the corresponding pressure of 35·8 atm. The molecular heat of sublimation has been calculated to 33·6 Cal., the molecular heat of vaporisation of the liquid is 11·2 Cal., and the molecular heat of fusion is 22·4 Cal. Attempts to measure the vapour pressure of the black modification of arsenic failed owing to the rapid conversion of this substance into the grey modification at the temperature of the experiment. J. F. S.

Preparation of Anhydrous Halides. GIUSEPPE ODDO and UGO GIACHERY (*Gazzetta*, 1923, **53**, i, 56—63).—Oddo and Serra (A., 1900, ii, 74) showed that arsenic, antimony, and bismuth trichlorides may be readily prepared by heating the corresponding oxides in a reflux apparatus with sulphur monochloride. In the modification of this method now proposed, arsenic trichloride is obtained by passing a stream of chlorine through a heated mixture

of arsenious oxide and powdered sulphur. The tribromide and triodide are prepared by heating a mixture, in stoicheiometric proportions, of arsenious oxide with sulphur and the halogen. The preliminary preparation of the sulphur monochloride is thus avoided.

T. H. P.

Preparation and Properties of Pure Graphite. M. PIRANI and W. FEHSE (*Z. Elektrochem.*, 1923, **29**, 168—174).—Filaments of artificial silk were carbonised under slight tension for about twenty hours in an atmosphere of coal gas, the final temperature attained being 500°, and then at 2200—2500° in hydrogen. The ash content of the resulting filaments was about 0·3%. The filaments were then made incandescent at temperatures ranging from 1500° to 2000°, when surrounded by either gaseous or liquid carbon compounds. The former included hexachlorobenzene at 3 mm. mercury pressure, light petroleum under pressure of 3 to 30 mm. mercury, and carbon tetrachloride at 15 mm. pressure. The liquids used included light petroleum and carbon tetrachloride. Graphite was by this treatment deposited on the filaments, until their diameters were from 0·2 to 0·3 mm., corresponding with 200 to 300 times their initial diameters. The filaments were finally heated for about half an hour at about 3500° in carbon monoxide. The chemical, crystallographic, mechanical, thermal, and electrical properties of the resulting filaments are detailed, attention being directed more particularly to the fact that the filaments can be bent like lead. J. S. G. T.

Some Properties of Graphite. R. M. BURNS and G. A. HULETT (*J. Amer. Chem. Soc.*, 1923, **45**, 572—578).—The densities of natural graphites from Ceylon, Alabama, and Pennsylvania, Acheson electrode graphite, and carbon produced by the explosion of graphitic acid, have been determined by the liquid immersion method. The density of pure natural graphite is about 2·20 and that of Acheson graphite about 2·30. Carbon produced by the explosion of graphitic acid has a density of 2·215, and is therefore probably graphite. Samples of graphites originally showed no drift or increase in weight with time after immersion in the liquid. The natural graphites, however, after being swelled, or increased in volume by treatment with fuming nitric acid and heat, showed remarkable drifts. Pressure was used to hasten the completion of the drift. The tendency to drift was largely destroyed by a severe compression of the swollen material previous to the determination of density. J. F. S.

Oxidation Processes by Means of the Carbon Model. O. MEYERHOF and H. WEBER (*Biochem. Z.*, 1923, **135**, 558—575).—The authors have studied the self-oxidation of charcoal in alkaline solution. Animal charcoal suspended in dilute alkali takes up oxygen continuously with formation of carbon dioxide. The velocity of oxidation is increased 60% by replacing the air by oxygen. The respiratory quotient (*RQ*) lies in all cases between 0·5 and 1·0 and the heat evolved is 4 cal. per c.c. of oxygen used.

The temperature coefficient for a 10° rise of temperature is about 1·75. The self-oxidation is a surface effect and is inhibited by various urethanes to different extents; the inhibition is due to displacement of the adsorbed substance from the surface, the adsorbed hydroxyl-ion being uninfluenced. The degree of oxidation is proportional to the amount of hydroxyl-ion adsorbed. Among the usual physiologically important units, only the amino-acids are rapidly oxidised by charcoal. Hexose-phosphoric acid is slightly oxidised to carbon dioxide, but dextrose, lævulose, and lactic acid are not. H. K.

The Structure of Silicon. HANS KÜSTNER and H. REMY (*Physikal. Z.*, 1923, **24**, 25—29).—*X*-Ray analyses of the respective crystal structures of five varieties of silicon containing from 2·7 to 72% of silica indicate that all conform to the diamond type of structure previously found by Debye and Scherrer (*ibid.*, 1916, **17**, 277). The length of side of the elementary cubical crystal cell is 5·4204±0·00016 Å. The *X*-ray spectrum of "amorphous" silicon containing 72% of silica was identified with that of natural quartz. In all cases, spectra having sharp lines were obtained. The different chemical activities of varieties of silica are due solely to differences in the ratio of surface to mass of the sample. J. S. G. T.

The Ammines of Silicic Acid. ROBERT SCHWARZ and ADOLF MATHIS (*Z. anorg. Chem.*, 1923, **126**, 55—84).—The only ammine of silicates described in the literature is $CuO,2SiO_2,2NH_3$ by Schiff, but the method of preparation and the analysis given are not satisfactory. The present authors describe the preparation of the metasilicates of copper, silver, zinc, lead, nickel, and cobalt. Analysis gave too high values for the SiO_3-ion, this being attributed to adsorption of silica from solution; precipitation from very dilute solutions is advisable. The following ammines were prepared: $CuSiO_3,2H_2O,NH_3$; $CuSiO_3,H_2O,NH_3$; $CuSiO_3,2H_2O,2NH_3$ (at −16°); $Ag_2SiO_3,2H_2O,2NH_3$; $ZnSiO_3,H_2O,NH_3$; $2PbSiO_3,2H_2O,NH_3$; $NiSiO_3,H_2O,NH_3$; $CoSiO_3,H_2O,NH_3$. The addition, therefore, is confined to one or two molecules of ammonia. It is only in the case of the copper salt that cooling increases the number of molecules of ammonia added; in other cases, the cooling merely accelerates the addition. Attempts to add ammonia to the anhydrous salts did not succeed, hence the molecular bound water is regarded as an essential part of the silicates, which influences their chemical reactions. Anhydrous zeolites, however, unite with ammonia readily. W. T.

Separation of Radium from Other Elements. U. CIALDEA (*Gazzetta*, 1923, **53**, i, 42—48).—To recover radium bromide accidentally dropped on the pavement, the sweepings and washings of the pavement were evaporated on a water-bath and the residue was mixed and fused with a mixture of 2 parts of sodium carbonate, 2 parts of potassium carbonate, and 1 part of sodium nitrate. These salts carry into solution the radium, which may then be

recovered completely by the precipitation of barium sulphate, this being accompanied by total precipitation of the radium. Radium is also precipitated, to some extent, together with silica, with the sulphur of ammonium polysulphide, etc.; ferric salts are reduced to the ferrous condition by radium. T. H. P.

Electrolytic Production of Alkali Chlorates, Employing Magnetic Iron Oxide as Anode. G. Grube and F. Pfunder (*Z. Elektrochem.*, 1923, **29**, 150—163).—When neutral solutions of alkali chlorides are electrolysed with a view to the production of chlorates, employing magnetic iron oxide as anode, the current efficiency of the process is less than when a platinum anode is used, partly owing to catalytic decomposition at the anode of the hypochlorous acid produced to hydrochloric acid and oxygen. In acid solution at from 60—70°, with an anode current density of from 0·01 to 0·015 amp. per sq. cm. employing a magnetic iron oxide anode, the yield of chlorate is 85% to 90% of the theoretical value calculated from the current. The process of electrolysis of solutions of alkali hypochlorites and of free hypochlorous acid is the same, whether a platinum or magnetic iron oxide anode be employed. In cold, neutral solution, the main electrolytic process is represented by $6ClO'+3H_2O+6\oplus \longrightarrow 6H^{\cdot}+2ClO_3'+4Cl'+3O$. In hot acid solutions, chlorate is produced principally in accordance with the secondary reaction $2HClO+NaClO \longrightarrow NaClO_3+2HCl$.

J. S. G. T.

The Hydrogen Sulphates of the Alkali Metals and Ammonium. Horace Barratt Dunnicliff (T., 1923, **123**, 731—738).

Electrolytic Preparation of Alkali Permanganate by Anodic Solution of Maganese under the Influence of Superimposed Alternating Current. G. Grube and H. Metzger (*Z. Elektrochem.*, 1923, **29**, 100—105).—The electrolytic preparation of potassium permanganate by the anodic solution of metallic manganese in a solution of potassium carbonate has been investigated, and it it found that at the ordinary temperature the process takes place with a very unsatisfactory current yield (20·5—29·1%). The imposition of alternating current on the manganese anode improves the current yield, but only very slightly (32%). An increase in the current yield is found to occur with medium alternating current densities, whilst with a high alternating current density the current yield falls below that of the simple direct current electrolysis. The different actions brought about by the superimposed anodic alternating current are discussed, and it is shown that the favourable action of the alternating current in the preparation of potassium permanganate consists in the opposition of the alternating current to the removal of alkali from the anode layer. The reduction of the current yield with high alternating current densities depends on the depolarising action of this current, which results in the formation of manganate rather than permanganate. J. F. S.

Phase Relations in the System, Sodamide–Potassamide, as determined from Melting-point Curves. CHARLES A. KRAUS and EUSTACE J. CUY (*J. Amer. Chem. Soc.*, 1923, **45**, 712—715).—The melting-point diagram of the system sodamide–potassamide has been obtained by the method of thermal analysis. The diagram indicates the existence of a compound between one molecule of sodamide and two molecules of potassamide, $NaNH_2,2KNH_2$, having a transition point at approximately 120°. The eutectic between the compound and sodamide lies at a point corresponding with 33 mol.% of potassamide at a temperature in the neighbourhood of 92°. The flatness of the melting-point curve of the compound indicates that it is largely dissociated in the melted mixture.

J. F. S.

The Properties of Ammonium Nitrate. V. The Reciprocal Salt-pair, Ammonium Nitrate and Potassium Chloride. EDGAR PHILIP PERMAN and HORACE LEONARD SAUNDERS (T., 1923, **123**, 841—849).

Heteromorphism of Calcium Carbonate. Marble, Synthetic and Metamorphic. MAURICE COPISAROW (T., 1923, **123**, 785—796).

Heteromorphism of Calcium Sulphate. Alabaster and its Synthesis. MAURICE COPISAROW (T., 1923, **123**, 796—799).

Tricalcium Phosphate. ÉMILE LUCE (*J. Pharm. Chim.*, 1923, **27**, 214—216).—Tricalcium phosphate, when properly prepared and dried at 100°, should not lose more than 5% of its weight when incinerated at a red heat. Several samples examined by the author yielded up to 20% loss on ignition indicating the presence of hydrated dicalcium phosphate in the substance, which was confirmed by the relative solubility of the samples in water and in ammonium citrate solution.

W. P. S.

[Molecular Volumes of] The Selenides of the Metals of the Alkaline Earths. FR. A. HENGLEIN and R. ROTH (*Z. anorg. Chem.*, 1923, **126**, 227—236).—The linear relation between the molecular volumes of inorganic compounds of similar crystalline form and constant magnitudes characteristic of their kations or anions (A., 1922, ii, 260) is shown to hold also for the selenides of calcium, strontium, and barium. These selenides were made by reduction of the corresponding selenates in a rapid stream of dry hydrogen at 400° for the calcium compound, at 600° for the strontium compound, and at 500° for the barium compound. The essential condition for success is the removal of the water formed before it has time to decompose the selenide.

The selenides are microcrystalline, white solids of cubic habit, which become coloured on exposure to air and decompose in water. Their densities were determined in a volumenometer containing hydrogen, and the following values are recorded: calcium selenide, 3·57; strontium selenide, 4·38; barium selenide, 5·02. The distances between the atoms in the crystals are calculated

from the molecular volumes and shown to agree with Bragg's figures.

Attempts to prepare the corresponding tellurides were unsuccessful.

H. H.

The Structure of the Sulphides of Magnesium, Calcium, Strontium, and Barium. SVEN HOLGERSSON (*Z. anorg. Chem.*, 1923, **126**, 179—182).—The lattice constant and the lattice structure of these salts were examined by the Debye-Scherrer method. They are all cubic; the unit cube containing 4-4 atoms, *i.e.*, four molecules. The results are tabulated. W. T.

The Brittleness of Inter-metallic Compounds. G. TAMMANN and K. DAHL (*Z. anorg. Chem.*, 1923, **126**, 104—112).—Pure metals and mixed crystals are plastic, this being due to the presence of gliding surfaces; intermetallic compounds, on the other hand, are brittle, this being due to a decrease in the number of gliding planes and to an increase in the tendency to fracture. Inter-metallic compounds were investigated at different temperatures by subjecting them to a sudden blow and to a high pressure. The authors found that almost all the compounds at the ordinary temperature show gliding planes and fractures. No gliding planes were found in the case of the alloys $CuMg_2$, Fe_2Sb_3, $FeSb_2$, Zn_3Sb, ZnSb, and FeSi. Metallic compounds such as Cu_3Sn which are characterised by good cleavage lose this property at higher temperatures and they become plastic. All the compounds investigated become plastic at a temperature about 50° below their melting point. W. T.

The Roasting Reaction Process of Copper. Equilibria in the System Copper–Sulphur–Oxygen. W. REINDERS and F. GOODRIAAN (*Z. anorg. Chem.*, 1923, **126**, 85—103; cf. A., 1915, 773).—An application of the static method to the elucidation of the mechanism of the metallurgy of copper. W. T.

Composition of Copper Hydroxides. L. LOSANA (*Gazzetta*, 1923, **53**, i, 75—88).—The composition of the various hydrates of cupric oxide has been investigated by several methods, including that devised by Cohen for determining transformation points (A., 1894, ii, 340). The results obtained show that dehydration of normal cupric hydroxide takes place in two distinct ways, according as it occurs in presence of a liquid or with the dry compound. In the former case, the dehydration is marked by the formation of the definite compounds, $3CuO,H_2O$, $4CuO,H_2O$, and $8CuO,H_2O$. The loss in weight at various temperatures and the vapour-pressure curves show that loss of water by the dry compound is accompanied by formation of the above hydrates and, in addition, of $6CuO,H_2O$ and $7CuO,H_2O$. The compound $8CuO,H_2O$ loses water when heated to redness, but the magnitudes of the losses are not sufficiently constant to indicate the formation of further definite compounds.

The pronounced accelerating effect of alkali on the readiness with which the dehydration occurs is confirmed, and it is found that basic salts exert an opposite influence. In some instances, loss of

water, although with very low velocity, occurs at temperatures below the true temperatures of dehydration.

The various hydrates mentioned may be regarded as definite and moderately stable compounds. T. H. P.

Mercury Cleansing Apparatus. AUGUSTUS EDWARD DIXON and JAMES LYTTLE MCKEE (T., 1923, **123**, 895—897).

Separation of Mercury into Isotopes in a Large Apparatus. WILLIAM D. HARKINS and S. L. MADORSKY (*J. Amer. Chem. Soc.*, 1923, **45**, 591—601).—A partial separation of the isotopes of mercury has been obtained by evaporation in a vacuum in a large steel apparatus. A difference in density of four hundred and eighty parts per million between the light and heavy fractions is found, and the atomic weight of the fractions differs by 0·1 unit. This has been secured, without other cooling than that given by ice, in two hundred and sixty-eight hours of operation of the apparatus, which holds 2·5 kg. of mercury, together with thirty-seven hours of operation of the small glass apparatus used in earlier work (A., 1922, ii, 295). The weights of the end fractions were 3·8 g. for the heavy fraction and 4·4 g. for the light fraction. The increase in the atomic weight of the heavy fraction is 0·052, and the decrease in atomic weight of the light fraction is 0·440 unit. A multiple unit apparatus which would give the same separation in about thirty hours has been designed. A set of curves is given to show the relation between the increase in density of an isotopic mixture and the cut. These curves exhibit one curvature when the amount of the heavier isotope is less than 50%, and the opposite curvature when the amount is greater than 50% and a point of inflection when the heavier isotope constitutes exactly 50% of the mixture. When several isotopes are present, there may be several points of inflection in the curves. J. F. S.

Action of Mercuric Oxide on Sulphur Monochloride. GIUSEPPE ODDO and UGO GIACHERY (*Gazzetta*, 1923, **53**, i, 63—64).—The reaction, $2HgO + 2S_2Cl_2 = 2HgCl_2 + SO_2 + 3S$, occurring when mercuric oxide is added gradually to sulphur monochloride, proceeds with great rapidity and is accompanied by the development of a large amount of heat. The yield of mercuric chloride is almost theoretical. T. H. P.

Rare Earths. XIV. Preparation and Properties of Metallic Lanthanum. H. C. KREMERS and R. G. STEVENS (*J. Amer. Chem. Soc.*, 1923, **45**, 614—617).—Metallic lanthanum is best prepared by the electrolysis of fused lanthanum chloride in a graphite crucible which serves as cathode by a current of 40—50 amperes at 7—8 volts. Small quantities of potassium fluoride and sodium chloride were added to the fusion during the electrolysis to maintain proper fluidity. The metal, which usually contained some carbide, was washed with water to remove all adhering salts and carbide, and was then remelted in a graphite crucible under a flux of pure calcium chloride. The metal thus obtained was free from all other metals, and gave no odour of a carbide decomposition when treated with water.

When the electrolysis was carried out in iron crucibles, the product always contained this metal, but electrolysis with a tungsten cathode gave a metal which did not contain tungsten. Pure lanthanum is readily attacked even by dry air; it melts at 826°, and has the following physical properties: $d^{15°}$, 6·1598; Brinnell hardness (500 kg.), 37; heat of combustion 1645 cal. per g.; kindling temperature 445°. The pure metal is not pyrophoric. Its alloys with iron are much harder than the pure metal and are not pyrophoric. J. F. S.

Ceric Perchlorate. FR. FICHTER and ERNST JENNY (*Helv. Chim. Acta*, 1923, **6**, 326—329).—Dilute solutions of ceric perchlorate can be obtained by dissolving freshly precipitated ceric hydroxide in 50% perchloric acid, or by the interaction of ceric sulphate and barium perchlorate, but the best method is by the electrolytic oxidation of cerous perchlorate, using a 27% solution with 22% of free perchloric acid. In nine hours, using a current of 0·01 ampere per sq. cm. at 30°, more than 96% of the cerous salt is oxidised. When the orange-red solution is heated, it gradually decomposes, forming the cerous salt with evolution of oxygen. On dilution of the concentrated solution with water, a yellow, basic salt is precipitated. When only a slight excess of perchloric acid is present, a basic salt can be obtained by merely warming the solution on the water-bath. It was obtained, mixed with some cerous salt, in the form of aggregates of fine needles having the composition $Ce_2^{IV}O_3(ClO_4)_2,12H_2O$, the amount of water of hydration being, however, uncertain. E. H. R.

The Ternary System, Aluminium-Zinc-Tin. I. The Binary Systems, Tin-Zinc and Aluminium-Tin. E. CREPAZ (*Giorn. Chim. Ind. Appl.*, 1923, **5**, 115—122).—Thermal analysis of the system zinc-tin, gives results which agree with those of Heycock and Neville (T., 1897, **71**, 392) and indicate that these metals form no compounds, but that, at high temperatures at least, a solid solution exists containing about 5% of tin. With the system aluminium-tin, thermal analysis, micrographic examination, and measurements of the hardness yield results indicating the existence of neither compounds nor mixed crystals.

Measurements of the values of E of the cell $Zn_xSn_{(1-x)}|N-H_2SO_4|$normal calomel electrode, give $-0·28$ volt as the potential of pure tin with respect to hydrogen. In the neighbourhood of pure tin, the potential rises rapidly to that of zinc, this value being maintained almost constant for all the other alloys. For alloys highly concentrated in tin, solid solutions may be formed, but under the conditions employed not more than 5% (2·8 atom %) of tin can dissolve in the zinc (cf. Herschkowitsch, A., 1898, ii, 582).

Similar measurements have been made with the cells $Al_xSn_{(1-x)}|0·1N-KAl(SO_4)_2|$normal calomel electrode and $Al_xSn_{(1-x)}|10\%KCl|Al$. The results obtained confirm Kremann's statement that the potential of aluminium is greatly influenced by the previous treatment of the surface of the metal (*Z. Metallkunde*, 1920, **12**, 289). The value, $-0·827$ volt, for the potential with respect to

hydrogen of aluminium with a knife-scraped surface, agrees with Kremann's result. In all cases, the maximum value observed immediately after immersion of the metal diminishes rapidly to about 0·2 volt; such diminution cannot be ascribed to polarisation phenomena rather than to the formation of a surface layer. For aluminium–tin alloys, the potential throughout almost the whole range of concentration is virtually constant and higher than that of aluminium. On the assumption that the potential of alloys of the eutectic type is regulated only by that of the less noble metal, the potential of the aluminium in these alloys would be −1·139 volt. This value is sensibly below that obtained by Kremann with aluminium amalgams, namely −1·3 volts, and this author's suggestion that an aluminium–mercury compound, less noble than aluminium itself, is formed, is not applicable in the present case, as no compound or new crystalline form is detectable.

T. H. P.

The Fall in Conductivity of Aluminium Chloride during Melting and the Constitution of the Halides of Aluminium. WILHELM BILTZ and ARTHUR VOIGT (*Z. anorg. Chem.*, 1923, **126**, 39—53).—The molecular volumes of the solid aluminium halides do not show a linear relationship (cf. A., 1922, ii, 505), the abnormality being caused by the chloride. The molecular volumes of the molten halides, obtained from a determination of their densities at the boiling point, show a linear relationship when plotted against the molecular volumes of the solid potassium salts. The molecular state of aluminium chloride in the crystalline form differs from that of the molten salt, the molecules in the former being held together by stronger forces; this is also shown by its high melting point. The densities and molecular volumes determined were as follows. Aluminium chloride, molten d^{190} 1·33, mol. vol. 100, solid d^{25} 2·44, mol. vol. 54·7. Aluminium bromide, molten d^{265} 2·26, mol. vol. 118; solid d^{25} 3·01, mol. vol. 88·7. Aluminium of iodide, molten d^{382} 2·78, mol. vol. 147; solid d^{25} 3·98, mol. vol. 102·5.

The electrical conductivity of crystalline aluminium chloride increases with the temperature from a zero value to a maximum of 10^{-6} reciprocal ohms; on melting it suddenly falls again to zero, and increases gradually with increasing temperature to 10^{-7} reciprocal ohms. This is attributed to the ions Al^{+++} and $(AlCl_6)^{---}$ in the crystals; on melting these combine to form the molecules (Al_2Cl_6). The bromide and chloride of aluminium are non-conductors in the solid state.

W. T.

Basic Aluminium Sulphate. F. S. WILLIAMSON (*J. Physical Chem.*, 1923, **27**, 284—289).—The formation of basic aluminium sulphate has been investigated. It is shown that when 2—4 g.-mols of sodium hydroxide are added to 1 mol. of potassium alum, the precipitate has a constant composition which corresponds with the formula $Al_2(SO_4)_3,(Al_2O_3)_4,15H_2O$. The substance, $(Al[OH]_3)_4,H_2SO_4$, obtained by Schlumberger on adding five molecules of potassium hydroxide to 1 g.-mol. of potash alum is a mixture, because too large quantities of alkali hydroxide were added. The substance

$Al_2(SO_4)_3,(Al_2O_3)_4,15H_2O$ loses less than 10% of its water when kept over concentrated sulphuric acid at the ordinary temperature. Practically all the water is expelled by heating at 150°, but less than one-third of it is taken up again at lower temperatures, so the substance is not a reversible hydrate. J. F. S.

Anodic Formation of a Perchloride of Manganese. ALAN NEWTON CAMPBELL (T., 1923, **123**, 892—894).

General Colloid Chemistry. V. Connexion between Constitution and Stability of Iron Oxide Sols. WOLFGANG PAULI and GEORG WALTER (*Koll. Chem. Beihefte*, 1923, **17**, 256—293; cf. A., 1921, ii, 246, 700; 1922, ii, 149).—The constitution of ferric oxide sols which had been subjected to prolonged dialysis has been determined by physico-chemical analysis. The complexes increase in size on prolonged dialysis, due to an increase in the number of neutral ferric hydroxide molecules associated with them; this number in no case is less than about one hundred and forty. The number of elementary complexes per c.c., Z, has been calculated from the chlorine-ion concentration, C_{Cl}, the molecular weight, M, the density, δ, and the average-diameter, d, of the particles by means of the formula $Z=N\cdot C_{Cl}/1000$, where N is the Avogadro number and $d=2\sqrt[3]{3M/4\pi SN}$. The following values of the four sols examined are recorded: I. $33Fe(OH)_3,4{\cdot}5FeOCl{\cdot}FeO^{\cdot}/Cl'$, $M=4000$, $Z=9{\cdot}4\times10^{18}$ and $d(\mu\mu)$ 1·3; II. $60Fe(OH)_3,5FeOCl{\cdot}FeO^{\cdot}/Cl'$, $M=7000$, $Z=4{\cdot}4\times10^{18}$, $d=1{\cdot}6$; III. $70Fe(OH)_3,4FeOCl{\cdot}FeO^{\cdot}/Cl'$, $M=8000$, $Z=3{\cdot}0\times10^{18}$, $d=1{\cdot}7$; IV. $130{\cdot}5Fe(OH)_3,3{\cdot}5FeOCl{\cdot}FeO^{\cdot}/Cl'$, $M=14500$, $Z=3{\cdot}6\times10^{17}$, $d=2{\cdot}0$. These sols are evidently below the limits of ultramicroscopic visibility. On dilution, the sols undergo a slight reduction in size. The degree of dissociation calculated, for the three sols examined, by means of the ratio $C_{Cl}:n_{Cl}$, where n_{Cl} is the total chlorine concentration, is the same for all three cases. Investigation of changes brought about by ageing and by dilution, both of which result in an abnormal increase in the mobility of the colloidal ion and of the conductivity, shows that in both cases the change is due to the same cause, namely, an increase in the number of ions. The tendency to this change appears to become less the longer the sol is dialysed. The experiments show that ageing is a necessary condition for the formation of smaller particles. The addition of sulphates and similar salts to the sols causes coagulation, with the formation of insoluble precipitates. The anomalous action of typical electrolytes which only cause precipitation when they are present in concentrations nearly equivalent to that of the total chlorine is explained by an equilibrium between the free chlorine-ions and the chlorine bound in the complex. The precipitated sol is a complex double salt, a chloro-sulphate, which is rich in sulphate and poor in chlorine.

J. F. S.

The Recent Formation of Blue Basic Ferrous Ferric Phosphate (Vivianite) on and in the Clods of an Arable Soil. HERMANN KUNZ-KRAUSE (*Ber. Deut. pharm. Ges.*, 1923, **33**, 20—25).—A greyish-blue to dark blue coloration was found on, and

extending in some cases to a depth of several centimetres in, the clods of arable land in the neighbourhood of Dresden. The coloured material was soluble in hydrochloric acid, and both ferrous and ferric iron and phosphoric acid were found in the solution. The coloration is therefore ascribed to the presence of blue basic ferric ferrous phosphate (vivianite) formed from colourless ferrous phosphate, $Fe_3(PO_4)_2,8H_2O$, by oxidation in air. The conditions governing the formation of this substance from ferruginous minerals and phosphoric acid, produced probably by the oxidation of organic phosphorus, its transport in solution in carbonic acid, and its reprecipitation by oxidation to the blue basic compound in the soil, are discussed. G. F. M.

Comparison of the Atomic Weights of Terrestrial Nickel and Meteoric Nickel. II. Analysis of Nickelous Chloride. GREGORY PAUL BAXTER and FRANK ARTHUR HILTON, jun. (*J. Amer. Chem. Soc.*, 1923, **45**, 694—700).—The atomic weight of nickel has been redetermined with material of terrestrial origin and also with material extracted from the Cumpas meteorite. The determination with both kinds of material has been made by means of the ratios $NiCl_2 : 2Ag$ and $NiCl_2 : 2AgCl$, both being made nephelometrically. In the case of the ratio $NiCl_2 : 2Ag$, six determinations were made with terrestrial nickel, and the value of the mean ratio was found to be 0·600730, the extreme values being 0·600746 and 0·600715, whilst for four experiments with meteoric nickel the mean value is 0·600726, the extreme values being 0·600741 and 0·600716. In the case of the ratio $NiCl_2 : 2AgCl$ two experiments were made with terrestrial nickel, and the mean value was found to be 0·452118, whilst three experiments with meteoric nickel gave 0·452142 as the mean value of the ratio. The value of the atomic weight of nickel from both sources is therefore the same, namely, 58·70 (Ag=107·880, Cl=35·458). The mean of the present value and those of Richards and Cushman (A., 1899, ii, 488), 58·68, and Baxter and Parsons (*ibid.*, 1921, **43**, 507) is 58·69 (see also A., 1898, ii, 288). J. F. S.

Specific Gravity of Anhydrous Nickelous Chloride. Determination of the Specific Gravity by Displacement of Air. GREGORY PAUL BAXTER and FRANK ARTHUR HILTON, jun. (*J. Amer. Chem. Soc.*, 1923, **45**, 700—702).—The specific gravity of anhydrous nickel chloride has been determined by displacement of air and also by displacement of toluene. In the former case, the value 3·52 is obtained and in the latter 3·54. The latter value is to be preferred. The experiments also indicate that anhydrous nickel chloride does not adsorb appreciable quantities of air.

J. F. S.

Equilibrium in the Systems Nickel Chloride, Cobalt Chloride, Cupric Chloride–Hydrochloric Acid–Water. H. W. FOOTE (*J. Amer. Chem. Soc.*, 1923, **45**, 663—667).—The solubility of the chlorides of nickel, cobalt, and copper (cupric) has been determined at 0° in water containing various concentrations of

hydrochloric acid (0—40%). Cupric chloride has been similarly examined at 25°. The composition of the liquid and solid phases has been ascertained at each point, and it is shown that cupric chloride forms a single additive compound with hydrochloric acid, at 0°, namely, $CuCl_2,HCl,3H_2O$; nickel chloride yields a dihydrate and a tetrahydrate in addition to the usual hexahydrate, whilst cobalt chloride yields only a dihydrate in addition to the hexahydrate. J. F. S.

Constitution of Aqueous Chromic Acid Solutions. FRIEDRICH AUERBACH (*Z. anorg. Chem.*, 1923, **126**, 54).—In reference to Dhar's paper (A., 1922, ii, 382), it is stated that the dissociation constant of the first stage of ionisation of chromic acid is extremely large, but in the second stage it is only $4—8\times10^{-7}$. W. T.

The Hydrates of Molybdenum Trioxide. GUSTAV F. HÜTTIG and BRUNO KURRE (*Z. anorg. Chem.*, 1923, **126**, 167—175).—The existence of hydrates of molybdenum trioxide was investigated by means of the Huttig tensi-eudiometer (A., 1921, ii, 195). The yellow precipitate obtained from a nitric acid solution of ammonium molybdate was shown to be the dihydrate $MoO_3,2H_2O$. A monohydrate, MoO_3,H_2O, was also shown to exist. Adsorption compounds were also indicated (cf. A., 1922, ii, 773). No stable hydrates of chromium trioxide were indicated. W. T.

Production and Characteristics of the Carbides of Tungsten. MARY R. ANDREWS (*J. Physical Chem.*, 1923, **27**, 270—283).—The reaction between incandescent tungsten filaments and naphthalene vapour has been investigated. The occurrence of two inflection points in the resistance-composition curve shows the existence of two carbides of the composition W_2C and WC. The mechanism of the reaction is discussed, and it is shown that the main factors are the rate of diffusion of carbon through tungsten carbide as a function of the temperature, the vapour pressure, and the value of the quantity, E, that is, the fraction of the total number of molecules which strikes the filament. The approximate resistivities of W_2C are given for various temperatures, and the conductivity of a partly carbonised tungsten filament is shown to be the sum of the conductivities of its two components. A few experiments with other carbonising agents are mentioned, particularly ethyl alcohol and acetylene. The rate of carbonisation with ethyl alcohol is only about one-fifth that with acetylene. Experiments with benzene, toluene, anthracene, methane, and illuminating gas are described. The results show that almost any hydrocarbon vapour will react with incandescent tungsten to give carbides. A complete vapour-pressure curve for naphthalene from $-50°$ to $+200°$ is given, which is represented by the equation $P=P_0e^{-Q/RT}$, where Q is the latent heat of vaporisation; a few values for the vapour pressure of toluene at low temperatures are recorded which include the following: $-90°$, 3 bars, $-80°$, 31 bars, and $-70°$, 49 bars. Carbonised filaments heated in a vacuum decompose at rates depending on the temperature; above 2400° K

the rate of decomposition is moderately rapid. The carbon is volatilised without loss of tungsten, and this loss may be driven to completion at 2700° *K*, leaving metallic tungsten wires of the same conductivity as before carbonisation. J. F. S.

The Equilibrium of Tungsten and its Oxides with Hydrogen and Water Vapour; Carbon Monoxide and Carbon Dioxide and Oxygen. J. A. M. VAN LIEMPT (*Z. anorg. Chem.*, 1923, **126**, 226; cf. A., 1922, ii, 301).—The author points out a mistake in his previous paper which necessitates a recalculation of his results. The recalculated vapour pressures at 1773° are: $WO_2 \rightleftharpoons W+O_2$, $p=10^{-80}$; $2W_2O_5 \rightleftharpoons 4W+5O_2$, $p=10^{-7\cdot6}$; $4WO_3 \rightleftharpoons 2W_2O_5+O_2$, $p=10^{-49}$ atmospheres. The recalculated heats of reaction are: $W+O_2=WO_2+127{,}900$ cal.; $4WO_2+O_2=2W_2O_5+125{,}200$ cal.; $2W_2O_5+O_2=4WO_3+140{,}400$ cal. H. H.

The Preparation of Pure Tungsten Dioxide and Tungsten Pentoxide. J. A. M. VAN LIEMPT (*Z. anorg. Chem.*, 1923, **126**, 183—184).—The methods of preparation are based on the equilibrium of the oxides of tungsten with hydrogen and water vapour (cf. A., 1922, ii, 301). A stream of hydrogen is passed through water kept at 85° and then the mixture of hydrogen and water vapour passed over tungsten trioxide kept at 900°; the trioxide is thus reduced to the dioxide. If the water is kept at 97°, then the product is the pentoxide. The above temperatures for the water are those to give the necessary concentration of water vapour in the mixture (cf. Chaudron, A., 1920, ii, 379). W. T.

Isolation of the Oxide of a New Element. A Correction. ALEXANDER SCOTT (T., 1923, **123**, 881—884).

Bismuth Subnitrate. E. ISNARD (*J. Pharm. Chim.*, 1923, **27**, 216—217).—Certain samples of bismuth subnitrate examined yielded a reaction with Bougault's reagent indicating the presence of arsenic, but this element was not found to be present when the samples were submitted to the Marsh test. The impurity present which gave the reaction with the Bougault reagent was tellurium.
W. P. S.

Cobaltinitrites of Bismuth and Cadmium. S. C. OGBURN, jun. (*J. Amer. Chem. Soc.*, 1923, **45**, 641—645).—By simple double decomposition cadmium cobaltinitrite and three bismuthyl cobaltinitrites were obtained from the action of sodium cobaltinitrite on a saturated solution of cadmium sulphate or bismuth nitrate, respectively. The bismuthyl compounds, $(BiO)_3Co(NO_2)_6$, $(BiO)_3Co(NO_2)_5$ and $(BiO)_3Co(NO_2)_4$, were obtained from the mother-liquor by rapid filtration at the various stages of the precipitation. Their structures may be represented by Werner's co-ordination grouping, and resemble those of the compounds $[RuCl_4O_2]Cs_2$ (Howe, A., 1904, ii, 490) and $[OsCl_4O_2]Cs_2$ and $[OsCl_3O_3]Cs_2$ (Wintrebert, Thesis, Bordeaux, 1902, 82). The compound $(BiO)_3Co(NO_2)_4$ is the most stable; the compounds range from yellow to orange in colour, are insoluble in ether, and only sparingly soluble in alcohol. On

keeping either in solution or in the solid state, they are rapidly decomposed. They are very hygroscopic, and great care was necessary in the separation. *Cadmium cobaltinitrite*, $Cd_3[Co(NO_2)_6]_2$, was isolated from the mother-liquor by fractional crystallisation, and is a bright canary-yellow coloured compound. It is stable both in solution and in the solid form, slightly hygroscopic, insoluble in cold water, and only slightly soluble in alcohol or ether, but it dissolves readily in boiling water. J. F. S.

General Colloid Chemistry. VI. Analysis and Constitution of Colloidal Gold. I. ERNA KAUTZKY and WOLFGANG PAULI (*Koll. Chem. Beihefte*, 1923, **17**, 294—312).—A large number of experiments are described which were designed to establish the constitution and composition of colloidal gold. Carefully prepared and dried gold colloids were heated in a current of carbon dioxide and the loss of weight and amount of oxygen evolved ascertained. The results make it very probable that colloidal gold does not contain oxygen compounds. This result is confirmed by the fact that when coagulated gold precipitates are boiled with hydrochloric acid gold does not go into solution. Similar gold precipitates are shown to contain only the smallest traces of chlorine. From these results it is concluded that the colloidal particle contains neither an oxygen-containing aurate group nor the anion of the gold salt used in the preparation of the sol. From conductivity measurements, it is shown that colloidal gold of specific conductivity $25—30\times10^{-6}$ $ohms^{-1}$ is free from foreign electrolytes, and that such a solution contains kations in the concentration $2.5\times10^{-4}N$. The precipitates formed by the addition of magnesium sulphate and barium chloride, respectively, to gold sols have been analysed after thorough washing and shown not to contain foreign elements. Colloidal gold retains a quantity of water when dried at 100°, an amount which is estimated at one molecule to each sixty gold atoms, and this can be accounted for on the assumption of an aquo-complex in the sense of Werner's hypothesis. The colloids examined in the present work were prepared by the action of tannin on solutions of gold chloride. J. F. S.

The Preparation of Ruthenium Pentoxide. HEINRICH REMY (*Z. anorg. Chem.*, 1923, **126**, 185—192).—Ruthenous hydroxide is extremely unstable and undergoes spontaneous oxidation to the pentoxide; the pentoxide is also obtained by keeping the tetroxide in a sealed tube for some time. The product in each case contains water; whether this is to be regarded as combined water has not been investigated. It would seem that ruthenium can exert any valency from one to eight. W. T.

Mineralogical Chemistry.

Mendeléevite, a New Radioactive Mineral. V. I. Vernadski (*Compt. rend.*, 1923, **176**, 993—994).—This was described in Russian in 1914 as a calcium urano-titanocolumbate. It occurs with orthite in pegmatite veins at Uluntui, near Slyudianka, Lake Baikal, Siberia. The greyish-black cubic crystals (rhombic dodecahedra with small octahedral faces) have a dull surface with semimetallic lustre and reddish-brown streak; *d* 4·76 (4·46 for larger crystalline masses), *H* 4½. It contains U_3O_8 23·5, CaO 15%, some lead, and little iron and rare-earths. It belongs to the betafite group (A., 1913, ii, 232); but whilst the yellowish and greenish colours of betafite suggest the presence of uranyl or uranium trioxide, the reddish-brown colour of the new mineral suggests the presence of the dioxide. Columbates and tantalates have not originated in the superficial deposits of the earth's crust (biosphere), and in this situation they are very stable. L. J. S.

Analytical Chemistry.

Drying and Weighing in Micro-analysis. A. von Szent-Györgi (*Biochem. Z.*, 1923, **136**, 102—106).—In using the Pregl micro-weighing tube and filter with asbestos, the difficulty was encountered that constancy of weight was not attained owing to the hygroscopic nature of the asbestos. This has been surmounted to a large extent by slightly modifying the Pregl tube by having the stem made of capillary bore and the top opening closed by a ground glass cap. The whole can be dried in an oven, a vacuum being applied to the capillary stem and the ground glass joint leaking sufficiently to allow a slow stream of air to pass. A suitable oven for a battery of tubes and a micro-thermo-regulator are also described. H. K.

The Effect of Alcohol on the Sensitivity of Colour Indicators. I. M. Kolthoff (*Rec. trav. chim.*, 1923, **42**, 251—275).—Indicators of acid character are more sensitive towards hydrogen-ions in presence of alcohol, those of basic character less sensitive, but Congo red is an exception. Alteration of temperature has the reverse effect on an indicator in alcoholic solution to that which it exerts in aqueous solution; the magnitude of the variation from neutrality in alcoholic solution as determined for various indicators changes rapidly with temperature. Different indicators exert maximum or minimum ratios of sensitivity with alteration of the alcohol content of a solution, and the existence of these maxima or minima is determined by the influence of the alcohol in decreasing the dissociation of the acid or basic indicators and the ionisation of the water. H. J. E.

Weighing Tube for Combustion Boats. RICHARD LANT (*Chem. Ztg.*, 1923, **47**, 258).—The apparatus consists of a glass tube closed at both ends with glass stoppers and mounted horizontally on a glass foot; a projection on the upper side of the tube serves as a handle. W. P. S.

New Method for the Electrolytic Separation and Estimation of the Halogens. GÉZA SCHAY (*Z. Elektrochem.*, 1923, **29**, 123—126).—The conditions under which the halogens may be separated and estimated electrolytically have been investigated. It is shown that the halogens may be separated in the free state under the following conditions. The separated halogen must be removed by boiling immediately it is liberated; the cathode must, with respect to the anode, have a surface as small as possible, so that the cathodic reduction of the halogen is repressed to the minimum. Based on these conditions, a process is described whereby bromine and iodine may be quantitatively estimated and the three halogens separated. The method is accurate; the error is generally below 0·1% and rarely exceeds 0·2%. J. F. S.

Electrometric Titration of the Halides in the Presence of One Another. H. H. WILLARD and FLORENCE FENWICK (*J. Amer. Chem. Soc.*, 1923, **45**, 623—633).—The electrometric titration of the halogens has been investigated. It is shown that the direct titration of bromide in hydrocyanic acid solution to cyanogen bromide, BrCN, by potassium permanganate is too slow to be used with the bimetallic electrode system. If, however, the usual monometallic system is used and the titration curve plotted, the end-point may be quite easily determined. The oxidation takes place in accordance with the theoretical requirement of two equivalents of oxygen, and the oxalate factor for the permanganate may be used in the calculations. The maximum in the $\Delta E/\Delta V-V$ curve described usually lies a little too far to the right, but when a correction of $-0·10$ c.c. of $0·1N$ titrating solution is made the maximum error is less than 0·4 mg. of bromine. A sub-maximum often precedes the end-point maximum in the $\Delta E/\Delta V-V$ curve, and the intervening sub-minimum lies extremely close to the theoretical end-point. The sub-maximum does not always show. Iodide if present is oxidised to the corresponding iodine compound, ICN, but chloride in any quantity does not interfere with the reaction. Since a selective determination of iodide is possible, the proposed method provides an excellent means for the rapid estimation of bromide in the presence of any concentration of the other two halides. Iodide may be accurately titrated electrometrically by oxidation to cyanogen iodide with permanganate in hydrocyanic acid solution in all concentrations of chloride and in moderate concentrations of bromide. The effect of the bromide is a function of the ratio of its concentration to that of the iodide, and also of the absolute concentration of each. A more accurate method is the oxidation of iodide to iodate by an excess of alkali hypobromite, the excess being titrated electrometrically with arsenite. In this case, the presence of any amount of bromide

or chloride is without effect. Either the bimetallic or monometallic electrode system may be used in both methods. J. F. S.

Rapid Estimation of Total Iodine in Mineral Waters containing Sulphides. J. DUBIEF (*Ann. Falsif.*, 1923, **16**, 80—82).—The sulphides and organic matter are oxidised with alkaline permanganate and the halogens then liberated by acidifying with sulphuric acid and dissolved in carbon disulphide. The excess of permanganate is removed with hydrogen peroxide. If the weight of bromine is less than five times that of the iodine, it does not interfere with the colorimetric estimation of the iodine in the carbon disulphide solution, and this can be immediately proceeded with. If more than this proportion of bromine is present, bromides of iodine are formed and the colour of the carbon disulphide solution becomes yellow. $N/10$-Potassium thiocyanate solution is then added drop by drop with agitation until the yellow colour disappears and the solution becomes violet. By this means 0·05 mg. of potassium iodide can be detected mixed with two thousand times its weight of the bromide. The solution should not contain more than 0·5 mg. of iodine, or the coloration is too intense for exact comparison. The iodine solution must be carefully cooled to avoid loss by sublimation. H. C. R.

Use of Phosphorus in Gas Analysis. AUGUST HOLMES (*Ind. Eng. Chem.*, 1923, **15**, 357).—Phosphorus has not the disadvantages attendant on the use of pyrogallol for oxygen absorption, but its action is sometimes a little slow, particularly in the case of gas engine exhausts and the residue from an explosion in gas analysis. By passing such gases through bromine water, however, the oxygen is activated and easily absorbed. It is not necessary to pass the gas after this treatment through alkali hydroxide, since no change in reading takes place. If the room is cold bromine inoculation likewise assists absorption of the oxygen by phosphorus. If the phosphorus has been contaminated by the illuminants or by the cuprous chloride, the black spots may be removed by displacing the water with concentrated nitric acid, or nitric and hydrochloric acids, and then removing the acids by displacement with water. The phosphorus will then be light in appearance and very active for some time. G. F. M.

Electrometric Estimation of Sulphur in Soluble Sulphides. H. H. WILLARD and FLORENCE FENWICK (*J. Amer. Chem. Soc.*, 1923, **45**, 645—649).—When the bimetallic electrode system previously described (this vol., ii, 33) is used, the end-point in the electrometric titration of sodium sulphide with an ammoniacal silver solution is unusually sharp. The *E.M.F.* rises slowly and sometimes irregularly at first, then there is a rise of 200—400 m. volts just before the end-point is reached, after which the completion of the reaction is marked by a very abrupt fall in potential. There is often a reversal of polarity during the titration which makes the first part of the rise apparently a fall. The proposed method is based on the reaction used by Lestelle (*Compt. rend.*,

1862, **55**, 739), in which the sulphide is precipitated as silver sulphide in alkaline solution by titration with standard ammoniacal silver solution. It is, however, much more simple and accurate than his visual determination of complete precipitation. The change of *E.M.F.* at the end-point is so great that it is quite unnecessary to plot the curve. The method is very accurate, and may be carried out in the presence of sulphite, sulphate, chloride, thiosulphate, and polysulphides. The estimation of sulphur in steel by this method is carried out as follows: a 10 g. sample of the steel is placed in a 250 c.c. flask connected through a condenser with a hydrogen generator, a dropping funnel for admitting acid and a "10-bulb tube" containing 100 c.c. of a 10% sodium hydroxide solution. The apparatus is swept out with hydrogen, 100 c.c. of hydrochloric acid (*d* 1·1) are added, and when the rapid evolution of hydrogen abates the solution is boiled. The stream of hydrogen is continued for five minutes after the steel has dissolved. The sodium hydroxide solution is then washed into a beaker and titrated with standard ammoniacal silver solution as described above.

J. F. S.

Estimation of Sulphur in Organic Compounds. WALTER F. HOFFMANN and ROSS AIKEN GORTNER (*J. Amer. Chem. Soc.*, 1923, **45**, 1033—1036).—The Benedict-Denis method for estimating sulphur in urine may be used to estimate sulphur in all kinds of organic compounds, excepting those which are volatile, and so escape before the thermal decomposition of the nitrates commences.

W. S. N.

Colorimetric Estimation of Traces of Thiosulphate in the presence of Sulphite. O. HACKL (*Chem. Ztg.*, 1923, **47**, 266).—Thiosulphate may be conveniently estimated colorimetrically after the addition of silver nitrate when the concentration lies between 0·1 mg. and 2 mg. per 100 c.c., expressed as S_2O_3. If sulphite is present, the solution may be acidified with a few drops of dilute sulphuric acid before the addition of the silver nitrate, without affecting the results of the colorimetric comparisons. Standards for comparison are prepared by adding a solution containing 0·1 mg. of S_2O_3 per c.c. to a volume of water equal to that of the sample being analysed. The solutions should be left for about five minutes before the comparison is made. H. C. R.

Estimation of Trithionates in the Presence of Tetrathionates. E. H. RIESENFELD, E. JOSEPHY, and E. GRÜNTHAL (*Z. anorg. Chem.*, 1923, **126**, 281—284; cf. A., 1922, ii, 45).—A method of estimation of trithionates in the presence of tetrathionates is described in which advantage is taken of the fact that trithionates react quantitatively with copper sulphate to produce copper sulphide according to the equation: $S_3O_6'' + Cu^{\cdot\cdot} + 2H_2O = CuS + 2SO_4'' + 4H^{\cdot}$. Tetrathionates were found to be indifferent to this reagent, thus confirming the work of Kurtenacker and Fritsch (A., 1922, ii, 521).

To a solution of about 0·1 g. of the salt to be estimated is added

50 c.c. of a solution of 10 g. of copper sulphate crystals in 200 c.c. of water acidified with 10 c.c. of dilute sulphuric acid (30 c.c. of strong acid made up to 100 c.c.). The reaction mixture is maintained at 70° for one day, at the end of which time the copper sulphide is filtered, ignited, and weighed as copper oxide. Experimental results are quoted to show that the method is trustworthy for mixtures of potassium tri- and tetra-thionates containing from 0 to 100% of the latter. H. H.

Estimation of Nitric Nitrogen and Total Nitrogen in Plant-tissue Extracts. PATRICK H. GALLAGHER (*J. Agric. Sci.*, 1923, **13**, 63—68).—An examination of methods for the estimation of nitrates by reduction to ammonia is described and a method depending on reduction with Devada's alloy and distillation with magnesia recommended. In plant extracts, colloidal matter is first removed by precipitation with an equal volume of alcohol. A portion containing nitrate approximating to 0·1 g. of potassium nitrate is distilled in steam with 1 g. of Devada's alloy and 0·5 g. of magnesia for forty-five minutes. An air-cooled reflux still-head is suggested to regulate the concentration of ammonia solution reaching the receiver. In Kjeldahl estimations where nitrates are present, the latter may be reduced by the addition of 1 g. of Devada's alloy and 2 c.c. of 25% sodium hydroxide solution. The ammonia is distilled off for thirty minutes and added to that finally found after digestion of the residue with sulphuric acid. Blank determinations with magnesia are necessary. A. G. P.

Volumetric Estimation of Small Amounts of Phosphorus, using a Standard Solution of Methylene-blue. WILLIAM M. THORNTON, jun., and H. I. ELDERDICE, jun. (*J. Amer. Chem. Soc.*, 1923, **45**, 668—673).—An oxidimetric process for the estimation of small amounts of phosphorus has been satisfactorily worked out, which depends on the formation of the ammonium phosphomolybdate precipitate, dissolution of this compound in ammonium hydroxide, reduction of the solution to molybdenum trichloride by hydrochloric acid and zinc in an air-free atmosphere, and titration to molybdenum pentachloride with a standard solution of methylene-blue, on the assumption that the ammonium phosphomolybdate has the normal composition $(NH_4)_3PO_4,12MoO_3,nH_2O$. The presence of iron does not interfere with the reaction. The solution of methylene-blue used contains about 4 g. per litre, and is standardised by means of a solution of titanous sulphate in hot hydrochloric acid solution. The solutions titrated must not contain much molybdenum or the end-point will not be observed sharply enough. The colour changes during the titration are salmon pink $\longrightarrow$ light yellow $\longrightarrow$ light green $\longrightarrow$ dark green; the final colour change indicates the end of the reaction. The method has been applied to the estimation of phosphorus in steel with satisfactory results. J. F. S.

Estimation of the Supposed Assimilable Phosphoric Anhydride in Soil. CIRO RAVENNA (*Giorn. Chim. Ind. Appl.*, 1923, **5**, 129).—After extraction of the soil with 1% citric acid solution,

the filtered liquid is evaporated to dryness and the residue oxidised with concentrated nitric acid in presence of a little manganese carbonate. The phosphoric acid is then estimated as usual by the molybdate method. [Cf. *J.S.C.I.*, 1923, May.] T. H. P.

Detection of Minute Quantities of Arsenic. II. O. BILLETER (*Helv. Chim. Acta*, 1923, **6**, 258—259).—In the method previously described for the detection of minute quantities of arsenic (A., 1919, ii, 32) the hypochlorous acid used for the elimination of hydrochloric acid may be replaced with advantage by fuming nitric acid. The current of hydrogen chloride containing the arsenic is received into 4—5 c.c. of nitric acid, and on evaporation a residue of arsenic acid is obtained which can be introduced directly into the Marsh apparatus. The method is sensitive to one millionth of a milligram. E. H. R.

The Replacement of Bettendorf's Reagent by Hydrochloric Acid and Calcium Hypophosphite Solution. E. RUPP and E. MUSCHIOL (*Ber. Deut. pharm. Ges.*, 1923, **33**, 62—64).—Bettendorf's reagent for arsenic can conveniently be replaced by a reagent prepared by dissolving calcium hypophosphite in 10 parts of hydrochloric acid (*d* 1·126). This reagent is equally sensitive, giving in all cases a very distinct brown coloration or precipitate within twenty minutes with as little as 0·1 mg. of arsenious oxide when heated in a boiling water-bath with the substance to be tested. In strongly acid solution the reduction proceeds still more rapidly. Satisfactory freedom from arsenic is in general indicated if no darkening in colour is produced within a quarter of an hour. The precipitation of calcium sulphate or the presence of selenium does not interfere with the test. In presence of antimony, the sodium sulphide test is to be preferred. G. F. M.

The Estimation of Arsenic in Organic Compounds. R. STOLLÉ and O. FECHTIG (*Ber. Deut. pharm. Ges.*, 1923, **33**, 5—9).—A method of general applicability for the estimation of arsenic in arsenical organic compounds consists in destroying the organic matter by the Kjeldahl-Gunning method at a minimum temperature of 345—355°, and titrating the arsenic as arsenic or arsenious acid. 0·2 G. of the arsenical compound, 7 g. of potassium nitrate, and 15 c.c. of concentrated sulphuric acid are mixed in a 100 c.c. Kjeldahl flask with a neck 15 cm. long and 2·2 cm. wide, and heated for one hour, a further quantity of 1 g. of potassium nitrate is added, and the heating continued for a further half hour, when the above-mentioned temperature should have been attained, corresponding with a loss of 6—7 g. in weight. 3 G. of ammonium sulphate are then added in order to effect the destruction of excess of nitric and nitrous acids, and after heating for fifteen minutes the contents of the flask are diluted with 50 c.c. of water, and 1·5 g. of potassium iodide are added. After keeping for twenty minutes, the liberated iodine is titrated with $N/10$-thiosulphate without an indicator. As a check on the figure obtained, the solution is nearly neutralised with sodium carbonate crystals, rendered alkaline with sodium

hydrogen carbonate, and the arsenious acid titrated with $N/10$-iodine until a permanent yellow colour is obtained. G. F. M.

Estimation of Carbon and Hydrogen in Organic Compounds containing Arsenic and Mercury. M. FALKOV and GEORGE W. RAIZISS (*J. Amer. Chem. Soc.*, 1923, **45**, 998—1003).—The methods given are modifications of the method of Dennstedt.

For the analysis of organic arsenic compounds the wider part of the inner tube is 5—6 cm. longer than usual. The substance, mixed with sea sand if explosive, is placed in a porcelain boat; between this and the catalyst are inserted a porcelain boat containing red lead and a piece of broken porcelain. The red lead, prepared by heating lead peroxide in a current of oxygen after drying at 140°, reacts quantitatively with arsenic oxide, forming lead arsenate, which is stable at a high temperature. The analysis, which is performed in the usual manner, occupies at most two hours. Should poisoning of the catalyst occur, it may be revivified by boiling for about three hours with 20% nitric acid, washing with hot water, and drying.

Compounds containing mercury are placed in a porcelain boat between which and the catalyst are inserted (*a*) a boat containing a mixture of red lead and sea sand, (*b*) a boat containing silvered asbestos, and (*c*) a piece of broken porcelain. The asbestos is silvered by mixing with a solution of silver nitrate (90 g. in 100 c.c.), evaporating to dryness, breaking into pieces the size of a pea, and gradually heating to redness in a porcelain crucible. During the combustion, the manipulation of which is described in detail, the mercury forms with the silver an amalgam which is stable to oxygen at comparatively high temperatures. In addition to carbon and hydrogen, mercury may be estimated from the increase in the weight of the boat containing the silvered asbestos; it is shown that the results so obtained are more accurate than by the gravimetric method, and that the operation is much more rapid. The silvered asbestos may be revivified after each combustion by heating to a high temperature in a hard glass tube closed at one end; most of the mercury condenses in the sealed end of the tube, the remainder being trapped by means of a larger boat containing silvered asbestos, placed in the tube near the open end. W. S. N.

Simple Method for the Estimation of Carbon in Aqueous Liquids. E. FREUND and G. BOTSTIBER (*Biochem. Z.*, 1923, **136**, 142—144).—The method used is a modification of the Messinger method. The substance is oxidised by potassium permanganate and dilute sulphuric acid in boiling solution and the carbon dioxide absorbed in alkali in a Peligot tube. For some substances, for instance, uric, tartaric, and benzoic acids, one hour is sufficient for complete oxidation, but aspartic acid requires three hours and casein much longer. H. K.

Estimation of Carbon Monoxide with Iodine Pentoxide. R. KATTWINKEL (*Brennstoff-Chem.*, 1923, **4**, 104—105).—For the

estimation of small quantities of carbon monoxide, absorption in cuprous chloride is useless, but the reaction with iodine pentoxide ($I_2O_5+5CO=5CO_2+I_2$) may be employed. The pentoxide, which is best prepared by oxidising iodine with chloric acid and heating the iodic acid formed at about 200°, should, before use, be heated at 180° until it no longer loses free iodine or water. The estimation is carried out by passing the gas through a U-tube containing iodine pentoxide and glass wool and immersed in an oil-bath at 110—120°, at which temperature the reaction is rapid and quantitative. The iodine vapours are absorbed, without condensing, in a 10% solution of potassium iodide and the carbon dioxide in $N/10$-barium hydroxide. The iodine is titrated with $N/1000$-sodium thiosulphate and the barium carbonate converted into sulphate and weighed. The apparatus is finally swept out with air which has been purified by passing over heated copper oxide and through potassium hydroxide and sulphuric acid. With a gas containing 4—6% of carbon monoxide, the values obtained from the iodine liberated were high as compared with those found by absorption in cuprous chloride. By introducing a U-tube containing charcoal immediately before the pentoxide tube very concordant results were obtained from the iodine liberated and the barium carbonate formed, and these agreed closely with the cuprous chloride values. Iodine pentoxide is reduced by hydrogen sulphide, acetylene, ethylene, and, if present in quantity, *n*-pentane; methane has no action on it. Carbon monoxide is not absorbed by charcoal, whilst the latter removes all unsaturated compounds. A detailed survey of relevant literature is given. W. T. K. B.

A New Absorption Bottle for Carbon Dioxide and Moisture. WILLIAM E. MORGAN (*Ind. Eng. Chem.*, 1923, **15**, 266).—An absorption bottle, for use with solid absorbents, consists of a cylindrical glass bottle with a ground glass cap at the base. The inlet and outlet tubes are sealed through the glass at the top, and the latter extends inside to the bottom of the bottle. To charge the bottle for carbon dioxide absorption, it is set, bottom up, on its flat top, the requisite amount of soda lime is introduced, a cotton or perforated rubber diaphragm is inserted if desired, and the calcium chloride is added. The ground joint at the base is greased, the cap fixed on, and the bottle, when inverted, is ready for use. The total weight of the bottle, filled, is about 80 g. G. F. M.

Estimation of Carbonate in Mineral Waters containing Sulphides. F. TOUPLAIN and J. DUBIEF (*Ann. Falsif.*, 1923, **16**, 76—80).—The direct estimation of carbonate-ion in mineral waters by evaporation to dryness, liberation of carbon dioxide with sulphuric acid, and subsequent absorption with soda lime, gives inaccurate results in the presence of sulphides owing to variations of the equilibrium between the acids hydrogen sulphide and carbonic acid, oxidation of sulphur to strong acids and to the production of sulphur dioxide, which is weighed as carbon dioxide. The sulphides may be eliminated by agitating the water with a small excess of lead peroxide for about fifteen minutes and subsequently

adding hydrogen peroxide and warming at 45° for half an hour. The water is cooled, filtered, and the carbon dioxide liberated with a mixture of sulphuric acid (2 vols.) and concentrated potassium dichromate (1 vol.), by which any thiosulphates not already completely oxidised are transformed into sulphates and sulphuric acid. The carbon dioxide evolved is then free from sulphur dioxide.

H. C. R.

Detection of Peroxides and Per-salts. A. BLANKART (*Helv. Chim. Acta*, 1923, **6**, 233—238).—Peroxides can be distinguished from per-salts by their action on an alcoholic solution of *p*-aminophenol. When shaken with this reagent, alkali peroxides give a deep blue to black colour; barium peroxide gives the same reaction more slowly, whilst magnesium peroxide and per-salts do not react. When the proportion of alkali peroxide in the mixture of salts to be tested is small, the alcoholic solution does not become coloured, but after a short time dark specks appear in the white precipitate.

It is impossible to distinguish between the different per-salts in solution, since they are hydrolysed more or less rapidly, giving hydrogen peroxide. In carrying out tests, the finely powdered substance must be added to the reagent. Percarbonates give, in this way, with a 30% neutral potassium iodide solution, an instantaneous strong brown coloration. A slower reaction is given by perborates, perhydro-orthophosphates, persulphates or by a mixture of perhydrocarbonate or perhydrophosphate with a hydrogen carbonate. With silver nitrate solution (0·05*N*), percarbonate gives a yellow precipitate of silver percarbonate, whilst perhydrocarbonate gives at once a black precipitate of silver with evolution of oxygen, although this reaction is masked in presence of much carbonate, or percarbonate. Perborates when pure give no reaction, but when contaminated with sodium peroxide they give at first a brown precipitate of silver oxide followed soon by a rapid evolution of oxygen and formation of a silver precipitate. Persulphates react slowly as hydrolysis occurs, giving a violet colloidal silver solution. Freshly prepared aniline water is slowly turned brown by percarbonate and persulphate, more slowly by perborate, whilst sodium peroxide and perhydro-salts are without action. A hot alcoholic solution of cochineal is decolorised by percarbonate, more slowly by perborate. The per-salts may also be distinguished to some extent by the colour change effected in cobaltous hydroxide. Thus with cobalt nitrate solution, percarbonate gives a green precipitate; perhydrocarbonate a greyish-brown; perborate a bright brown, greyish-brown in presence of sodium carbonate; perhydropyrophosphate a blue, greyish-green in presence of carbonate; perhydro-orthophosphate, rose, turned brown by carbonate, and persulphate a rose colour turned violet by carbonate. E. H. R.

Estimation of Sodium Hyposulphite. R. W. MERRIMAN (*Chemistry and Industry*, 1923, **42**, 290—292).—A method described for the estimation of sodium hyposulphite depends on the fact that this substance, in the presence of excess of formaldehyde, forms sodium formaldehydesulphoxylate and formaldehyde sodium

hydrogen sulphite, $Na_2S_2O_4+2CH_2O+4H_2O=NaHSO_2,CH_2O,2H_2O+NaHSO_3,CH_2O,H_2O$. The formaldehyde sodium hydrogen sulphite is not acted on by iodine in neutral or acid solution, whilst the sodium formaldehydesulphoxylate may be titrated with iodine solution. The action of iodine on sodium hyposulphite solution containing excess of formaldehyde is shown by the equation:

$$Na_2S_2O_4+CH_2O+2I_2+4H_2O=NaHSO_4+4HI+NaHSO_3,CH_2O,H_2O.$$

Each c.c. of $N/10$-iodine solution is equivalent to 0·004352 g. of sodium hyposulphite. The details of the estimation are as follows. Twenty c.c. of 40% formaldehyde solution and 930 c.c. of water are placed in a litre flask, the neck of which is cut off 1 inch above the graduation mark; 10 g. of the sample are added while the contents of the flask are shaken, the solution is then diluted to 1000 c.c., the flask is closed, and shaken thoroughly for five minutes. Twenty c.c. of this solution are now added to 100 c.c. of water contained in a beaker, 50 c.c. of $N/10$-iodine solution are added, and, after two minutes, the excess of iodine is titrated with $N/10$-thiosulphate solution. W. P. S.

The Colorimetric Estimation of Calcium. ACH. GRÉGOIRE, E. CARPIAUX, E. LAROSE, and (MLLE) TH. SOLA (*Bull. Soc. chim. Belg.*, 1923, **32**, 123—130).—The method is based on observations of the pale yellow colour of the colloidal precipitate of calcium oleate obtained by the action of potassium oleate on the solution of a calcium salt in presence of potassium hydroxide and potassium sodium tartrate. When dilution is great, the excess of potassium oleate is hydrolysed and partly adsorbed on the precipitate. It is claimed that the method is practicable and of considerable accuracy. It is applicable only if the solution to be examined contains no other kation precipitated by potassium oleate under the same conditions. The presence of magnesium, if in quantities not greater than 30% of the calcium content, has no effect; beyond that proportion, the error due to magnesium increases rapidly with the proportion of that element. In these circumstances, an accurate estimation may be effected after preliminary separation of magnesium. Full experimental details are given. H. J. E.

Criticism of de Waard's Micromethod. KURT BLÜHDORN and GRETE GENCK (*Biochem. Z.*, 1923, **135**, 581—584).—The authors have tested afresh de Waard's micro-method for the estimation of calcium in small quantities of serum by direct precipitation as oxalate and find it suitable for clinical use, although entailing the use of the micro-balance. H. K.

Analytical Precipitation in Extreme Dilution. Barium Sulphate. FRIEDRICH L. HAHN; [with R. OTTO] (*Z. anorg. Chem.*, 1923, **126**, 257—268).—The author endeavours to overcome the well-known difficulty of complete precipitation of pure barium sulphate in the presence of other salts. This may be achieved in one of two ways: either by "precipitation in extreme dilution," by which he means the addition of the reacting solutions slowly

and at approximately equivalent rates to a small quantity of water or hydrochloric acid, thus securing very great effective dilution without undue increase of solution volume; or by heating the reagents in a sealed tube with hydrochloric acid to secure what is virtually a recrystallisation of the barium sulphate. Both methods give a coarsely crystalline precipitate of barium sulphate which is easily manipulated.

For the former method, about 20 c.c. of a solution containing about 9 g. of potassium sulphate per litre are allowed to flow simultaneously with a slight excess of an equivalent barium solution into 10 c.c. of boiling normal hydrochloric acid. The precipitate is filtered, washed, and weighed in the usual way. It is found that additions of potassium chloride up to 5 molecular proportions do not affect the results. Calcium chloride up to one molecule has no effect; up to two molecules, a slight effect, and thereafter, a marked effect on the results, but the error introduced in this way is much less than the error under the same conditions with the usual method. Potassium nitrate up to 4 molecules is practically without effect. Ferric chloride causes a large error and the precipitate is coloured, but by adding ammonia to the barium solution and carrying out the precipitation in water, subsequently removing the ferric hydroxide by washing with hydrochloric acid, the precipitate appears quite white and no appreciable error is introduced by the addition of 3 molecules of ferric chloride. Chromium chloride is treated in the same way as iron, and has no effect on the results when present in amounts up to 1·3 molecular proportions.

For the other method, the weighed sulphate is introduced into a tube with a slight excess of barium chloride and 2 c.c. of hydrochloric acid for every 100 mg. of barium sulphate. The tube is sealed and heated for three hours at 260°, when it is allowed to cool and the precipitate collected and weighed in the usual way. Longer heating or higher temperatures are unnecessary except when iron is present, when heating for three hours at 300° is requisite. Potassium chloride, calcium chloride, nitric acid, nickel and cobalt nitrates, iron, and aluminium chlorides are without effect on the results. It is shown that in the Carius method for the estimation of sulphur in organic compounds, it is unnecessary to remove the nitric acid by evaporation with hydrochloric acid provided that the barium chloride is introduced into the tube before heating. H. H.

The Colorimetric Estimation of Magnesium. ACH. GRÉGOIRE and (MLLE) TH. SOLA (*Bull. Soc. chim. Belg.*, 1923, 32, 131—136; cf. this vol., ii, 339).—Magnesium may be estimated with considerable accuracy by colorimetric measurement of the precipitate of oleate obtained by means of potassium oleate in presence of ammonia and ammonium chloride. The conditions are similar to those in the case of calcium, as are the limits within which the method may be applied. The simultaneous estimation of calcium and magnesium by this method is regarded as impracticable owing to the difference in colour of the two oleates and to the number of corrections involved. H. J. E.

Estimation of Small Quantities of Aluminium. L. K. Wolff, N. J. M. Vorstman, and P. Schoenmaker (*Chem. Weekblad*, 1923, **20**, 193—195).—The Alizarin-*S* method of Atack (A., 1915, ii, 842) was not found to be accurate, but good results were obtained by using the sodium compound of alizarin itself instead of the sulphonic acid. All other common metals and silicon interfere, and must be removed; special precautions must be observed in the use of glass vessels. S. I. L.

The Reaction between Manganese, Lead Peroxide, and Sulphuric Acid. E. I. Dyrmont (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1807—1814).—A modification of the Crum-Volhard reaction for the detection of manganese, which consisted in the addition of the substance to be tested to a boiling suspension of lead peroxide in nitric acid, when a violet coloration is produced. It is shown that the substitution of dilute sulphuric acid for nitric acid in the above reaction enhances the delicacy of the reaction. This method is not suitable for quantitative estimations, as the maximum amount of manganese capable of being oxidised in this way to permanganic acid is only 30%. Maximum oxidation is obtained using 8—9% sulphuric acid, greater or smaller concentrations causing a rapid decrease in the amount of oxidation. R. T.

The Mechanism of the Crum-Volhard and of the Dyrmont Reactions for Manganese. N. A. Valiaschko (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1815—1820; cf. preceding abstract).—A comparative study is made of the above reactions for the detection of manganese. It is shown that the Dyrmont modification of the Crum-Volhard reaction, which consists of substituting sulphuric acid for the nitric acid used in the latter, gives a much more intense coloration, which has the further advantage of being stable towards sulphuric acid, whereas the permanganic acid produced by the Crum-Volhard reaction is decomposed by prolonged boiling with nitric acid. This decolorisation is explained by Volhard, and by Morse (A., 1897, ii, 145), to be due to the precipitation of hydrated manganese dioxide, which is thus removed from the sphere of reaction. Hydrated manganese dioxide, however, is found to give the Crum-Volhard reaction for manganese, and the brown precipitates obtained by prolonged boiling of the reaction solutions in both cases are probably double compounds of lead peroxide and manganese dioxide. These compounds are not identical, the compound obtained from the Crum-Volhard reaction being more stable to acids than the substance obtained from the Dyrmont modification of this method, thus explaining the greater permanence of the coloration obtained by the latter. R. T.

Separation of Iron and Aluminium from Manganese and certain other Elements. G. E. F. Lundell and H. B. Knowles (*J. Amer. Chem. Soc.*, 1923, **45**, 676—681).—Moderate amounts of iron and aluminium can be separated from manganese and nickel as satisfactorily by precipitation with ammonium hydroxide solu-

tion as by the basic acetate or barium carbonate methods. The only requirements are those recommended by Blum for the complete precipitation of aluminium (A., 1916, ii, 493), namely, the presence of ammonium chloride, very low alkalinity (P_H=6·5—7·5, as indicated by methyl-red or other suitable indicator), and only one to two minutes' boiling of the alkaline solution. Phosphorus and vanadium interfere but slightly in the separation when iron or aluminium is present in preponderating quantity. When the reverse is the case, they form insoluble compounds with the manganese and interfere, not only in separations by ammonium hydroxide, but also in the methods using basic acetate or barium carbonate. Under the above conditions, the separation of iron and aluminium from cobalt, copper, and zinc is incomplete. A large excess of ammonium chloride improves the separation. An excess of both ammonium hydroxide and ammonium chloride improves the separation from copper and zinc. Under these conditions, however, the precipitation of aluminium is incomplete, and the separation from manganese, nickel, and cobalt is less satisfactory. J. F. S.

New Method of Detecting Nickel in Solution. C. G. VERNON (*Chem. News*, 1923, **126**, 200).—Excess of concentrated ammonia was added to the solution containing nickel, and hydrogen sulphide was passed through it for a short time. The solution was then boiled and a bright mirror of metallic nickel was deposited. The test is not affected by the presence of cobalt. H. C. R.

Estimation of Small Quantities of Molybdenum in Tungsten. WALKER J. KING (*Ind. Eng. Chem.*, 1923, **15**, 350—354).—Gravimetric methods for the estimation of molybdenum in tungsten are untrustworthy for quantities of less than 300 parts per million. For lesser proportions than this a colorimetric method is recommended depending on the formation of a blood red coloration of molybdenum thiocyanate when the alkali salts of tungsten and molybdenum are treated with an excess of hydrochloric acid in presence of tartaric acid, the solution treated with potassium thiocyanate, the molybdic acid reduced with stannous chloride, and the red coloured substance extracted with ether and matched against molybdenum standards prepared in a similar manner. A special modification of the Campbell and Hurley colorimeter is used for dealing with the volatile ethereal solutions, and a special flask made by fusing a 400 c.c. flask into the bottom of a 300 c.c. flask provided with a syphon, is used for the shaking-out process. None of the metals usually associated with tungsten ores interferes with the method, which is trustworthy for quantities of molybdenum as low as 10 parts per million of tungsten. The source of light for the colorimeter was standardised by using a 500 watt "Trutint" daylight unit. G. F. M.

Rapid and Sensitive Method for Detecting Bismuth in Urine. II. SERAFINO DEZANI (*Boll. Chim. Farm.*, 1923, **62**, 97—101).—The author replies to Ganassini's criticisms (this vol., ii, 93) and produces further evidence supporting his method of

detecting bismuth in urine, this being instantaneous and capable of detecting 1 part of bismuth in 1,000,000 parts of aqueous solution or in 500,000—600,000 parts of urine. T. H. P.

Estimation of Small Amounts of Ethyl Ether in Air, Blood, and other Fluids, together with a Determination of the Coefficient of Distribution of Ethyl Ether between Air and Blood at various Temperatures. HOWARD W. HAGGARD (*J. Biol. Chem.*, 1923, **55**, 131—143).—The method, which is not suitable for quantities of ether greater than 6 mg., has been developed for use in connexion with studies of ether anæsthesia, and depends on the oxidation of ether by iodine pentoxide at 200°, which proceeds according to the following equation:

$$5Et_2O+12I_2O_5=25H_2O+20CO_2+24I.$$

For the estimation, air, free from carbon monoxide, is drawn successively through a tower of calcium chloride, a bubbler containing the liquid to be analysed (heated at 40° during the later stages), a tower of solid potassium hydroxide, a U-tube filled with alternate layers of iodine pentoxide and glass wool and immersed in an oil bath at 200°, and finally an absorption tube containing a solution of potassium iodide. The iodine liberated is absorbed in the latter and is estimated by titration with thiosulphate. The result of a blank experiment must be deducted from the value so obtained. In order to render it suitable for use, the iodine pentoxide must be submitted to the preliminary treatment of heating it to 220—250° in a current of air for at least fifteen hours.

Using this method, estimations have been made of the distribution of ether between air and water and air and blood at various temperatures between 24° and 40°. E. S.

Estimation of Various Monohydric Phenols by the Phenol Reagent of Folin and Denis. CARLETON HENNINGSEN (*Ind. Eng. Chem.*, 1923, **15**, 406—407).—Monohydric phenols in dilute aqueous solution can be estimated by the phosphotungstic-phosphomolybdic acid reagent of Folin and Denis (A., 1915, ii, 802) with a fair degree of accuracy without the use of an empirical factor, but employing β-naphthol or *iso*amylphenol as standards, since the intensity of the blue coloration produced appears in the case of all monohydric phenols to be proportional to the molecular concentration of the phenol. The strength of the solution for the actual colorimetric test should not exceed about 0·5 mg. of phenol per 100 c.c., and after the addition of the reagent and the sodium carbonate solution the mixture is maintained at 30° for thirty minutes before comparing the tints in a Duboscq colorimeter.

G. F. M.

Analysis of "Sodium Cresylate." E. ISNARD (*J. Pharm. Chim.*, 1923, **27**, 217—220).—The following method is proposed for the estimation of the total cresols in sodium tolyloxide. One hundred g. of the substance are treated with 2 g. of calcium chloride, diluted to 150 c.c., and filtered; 100 c.c. of the filtrate are acidified with hydrochloric acid and extracted twice with ether. Ten g.

of sodium chloride are then dissolved in the aqueous liquor and the extraction with ether is repeated several times. The united ethereal extracts are washed with water, dried with anhydrous sodium sulphate, filtered, the ether is evaporated, and the residue of cresols heated at 80°, cooled, and weighed. W. P. S.

Gravimetric Micro-cholesterol Estimation. A. VON SZENT-GYÖRGI (*Biochem. Z.*, 1923, **136**, 107—111).—Windaus's cholesterol estimation by means of digitonin is carried out on 0·1 to 0·5 mg. of cholesterol using the modified filter tube previously described (this vol., ii, 330) and with an error for pure cholesterol of about 3%. H. K.

Micro-cholesterol Estimation by Titration. A. VON SZENT-GYÖRGI (*Biochem. Z.*, 1923, **136**, 112—118).—This method depends on the oxidation of the cholesterol-digitonin complex with hot chromic acid and titration of the excess of chromic acid by potassium iodide and thiosulphate. The micro-filtration tube described previously (this vol., ii, 330) is surrounded by a jacket through which steam can be blown so as to effect the oxidation in situ at 100°. H. K.

New Reactions for the Detection of Sterols. GEORGE STAFFORD WHITBY (*Biochem. J.*, 1923, **17**, 5—12).—(1) Two c.c. of a reagent consisting of a mixture of sulphuric acid and formalin in the proportions of 50 volumes to 1 are added to 2 c.c. of a chloroform solution of the sterol (preferably 1—2 mg. of the sterol) and shaken. After shaking, the upper chloroform layer is found to be cherry-red in colour, whilst the lower sulphuric acid layer is brownish-red in colour and shows an intense green fluorescence. On pouring off the upper layer and treating it with two or three drops of acetic anhydride a bright blue colour, which lasts for a considerable time but passes into a green within an hour, is produced. This reaction is more than ten times as sensitive as the Salkowski reaction.

(2) On the addition of 25 drops of a reagent made up by mixing concentrated sulphuric acid and formalin in the proportion of 50 vols.: 1 vol. to 2 c.c. of a solution of 0·2—0·5 mg. of the sterol in glacial acetic acid, a rose-coloured, fluorescent solution is obtained. This reaction is claimed to be more sensitive than any colour reaction hitherto used for the detection of sterols—the limit of sensitiveness of the reaction is 1 in 200,000.

(3) A few mg. of a sterol are added to 1 drop of acetic anhydride on a piece of porcelain and gently heated until it has melted and the excess of anhydride has been driven off. When completely cooled the fused mass is moistened with concentrated nitric acid, when the substance assumes a blue or bluish-green colour. This reaction is of value for cholesterol, but is not suitable for phytosterol.

A differential test for sterolins is also described. One to two c.c. of concentrated sulphuric acid are poured on to a few particles of a sterolin in a test-tube and the mixture is warmed gently to effect solution; on cooling, a cold saturated aqueous solution of thymol is poured on top of it. The lower layer shows an orange colour

with strong green fluorescence. A violet ring is formed at the junction of the layers. When kept, the violet colour tends to spread through the upper layer. With sterols, the same colour is obtained in the lower layer, but no violet ring appears. The author suggests that all reactions for sterols in solution are in their essential features similar. S. S. Z.

The Effect of Soluble Calcium Salts on the Estimation of Dextrose, and its Cause. WILHELM BIEHLER (*Z. Biol.*, 1922, **77**, 59—72).—In the estimation of dextrose by means of Fehling's solution, low results are obtained if soluble calcium salts are present, the error being approximately proportional to the quantity of calcium. Soluble salts of barium and strontium, but not of magnesium, zinc, or lithium, act similarly. This loss of reducing power is probably caused by the partial conversion of the dextrose into saccharinic acid under the influence of the alkaline-earth hydroxides. E. S.

Observations on the Method of Folin and Wu, and the Manganimetric Modification for the Estimation of Small Quantities of Reducing Sugar. PAUL FLEURY and LOUIS BOUTOT (*Bull. Soc. Chim. biol.*, 1923, 5, 148—152).—The shade and intensity of the blue colour produced in the Folin and Wu method varies with time, whilst the amount of potassium permanganate absorbed is more constant. W. O. K.

Electrometric Titration of Reducing Sugars. WANDA L. DAGGETT, ARTHUR W. CAMPBELL, and J. L. WHITMAN (*J. Amer. Chem. Soc.*, 1923, **45**, 1043—1045).—The sugar solution is added rapidly to the boiling Fehling's solution, the course of the reaction being followed by comparing the potential of a platinum electrode immersed in the Fehling's solution with that of a normal calomel electrode. After each addition of sugar, the deflection of a galvanometer in circuit with the titration vessel is noted; this deflection is at first small and irregular, becoming large at the end-point. Further additions of sugar produce relatively small deflections. The method, as checked gravimetrically, is found to be accurate. W. S. N.

The Estimation of Sugar in the Blood. EDWIN GEORGE BLEAKLEY CALVERT (*Biochem. J.*, 1923, **17**, 117—129).—A method based on Folin and Wu's and on Mackenzie Wallis and Gallagher's methods. The blood is collected in a platinum capsule which is introduced after weighing into a test-tube containing distilled water. The protein and other interfering substances are removed by the tungstic acid precipitation method of Folin and Wu and the cuprous oxide obtained with the reducing sugar is estimated colorimetrically with phospho-molybdic acid against permanent standards of coloured glass disks. A curve of correction for copper reductions is given. S. S. Z.

Estimation of Sugar by the Picric Acid Method in Liquids Poor in Protein. W. MESTREZAT and (MLLE) Y. GARREAU (*Bull. Soc. Chim. biol.*, 1923, **5**, 41—58).—The sugar present in such

liquids as the cerebrospinal fluid may be advantageously estimated by the method of Benedict and Osterberg (A., 1921, ii, 660). Details are given of a macro- and a micro-method of carrying out the estimation, and comparison of these methods with the Folin-Wu-Guillaume method shows good agreement. If too much creatinine or similar reducing substance be present, this must first be separated.

W. O. K.

Estimation of Lactose. VINCENT EDWARDS (*Chem. News*, 1923, **126**, 191).—In the volumetric estimation of lactose by means of Fehling's solution, the end-point of the titration is sharply defined if, in addition to a small quantity of magnesium tartrate, a piece of paraffin wax is added to the mixture of Fehling's solution and water. W. P. S.

The Iodometric Estimation of Aldoses. I. M. KOLTHOFF (*Pharm. Weekblad*, 1923, **60**, 362—375).—Aldoses are quantitatively oxidised to the corresponding carboxylic acids by iodine in alkaline solution. To the neutral sugar solution is added at least twice the theoretical quantity of iodine, and then with constant shaking not more than twice the theoretical quantity of sodium hydroxide; after five to ten minutes, the solution is acidified and the excess of iodine estimated by thiosulphate. Sodium carbonate may be used in place of the hydroxide, but the reaction is slower. By blank determinations under the same conditions, the amount of iodine taken up by other substances present may be allowed for. S. I. L.

Application of the Iodometric Estimation of Aldoses to the Analysis of a Mixture containing Carbohydrates. I. M. KOLTHOFF (*Pharm. Weekblad*, 1923, **60**, 394—402).—Lactose may be accurately estimated in milk by the iodine method (preceding abstract) after removal of proteins. In invert-sugar, honey, jam, and similar mixtures containing lævulose, dextrose, and possibly sucrose, the dextrose is estimated iodometrically without correction; the dextrose and lævulose are then estimated together by use of Fehling's solution, the lævulose so determined giving to the necessary accuracy the correction required for the iodine taken up by it in the iodometric estimation. The sucrose is then inverted, and the dextrose so formed estimated by another iodine titration, correcting for lævulose. If dextrin is also present, after the above procedure a more vigorous hydrolysis is carried out, and the dextrose so formed again estimated by difference. S. I. L.

Estimation of Formic Acid. E. O. WHITTIER (*J. Amer. Chem. Soc.*, 1923, **45**, 1087).—It is shown that in estimating formic acid by oxidation by means of alkaline potassium permanganate solution (Jones, A., 1895, ii, 463) at least twenty minutes are required for completion of the oxidation. W. S. N.

Characteristic Colour Reaction of Oxalic Acid and Oxalates. MULLER (*Bull. Assoc. Chim. Sucr.*, 1922, **40**, 169—171).—Ten c.c. of a solution of a small quantity of oxalic acid or an oxalate in

dilute sulphuric acid are treated in a test-tube with a few crystals of resorcinol and 2 c.c. of concentrated sulphuric acid are added so as to form a layer below the solution. A blue or bluish-green zone appears at the junction of the two liquids; on shaking the tube, the whole mixture is coloured blue, and this colour changes to violet when the mixture is heated slightly. Other organic acids yield yellow or red colorations with the test. W. P. S.

The Sulphuric Acid Test for Liver Oils. ARTHUR HARDEN and ROBERT ROBISON (*Biochem. J.*, 1923, **17**, 115—116).—The purple coloration given by liver oils on addition of a few drops of sulphuric acid can be simulated by adding the sulphuric acid to a light petroleum solution of cholesterol and furfuraldehyde or ω-hydroxymethylfurfuraldehyde. Chloroform may also be used as a solvent, but unless the solutions are carefully dried more sulphuric acid will be required to produce the coloration. The addition of furfuraldehyde to oils such as butter, which by themselves give only a faint reaction, causes the production of a very intense purple coloration on adding sulphuric acid. Attempts to obtain furfuraldehyde, or a compound which could replace it in this reaction from coal fish oil by distillation and other means failed. The above reaction can also serve as a delicate test for cholesterol; a faint purple colour is slowly developed with 0·1 mg. in 5 c.c. of light petroleum containing excess of furfuraldehyde. With 0·5 mg. of cholesterol, the reaction takes place immediately. S. S. Z.

Estimation of Lipoids in Blood and Tissues. III. PIERRE LEMELAND (*Bull. Soc. Chim. biol.*, 1923, **5**, 110—124).—A new method is described for the estimation of unsaponifiable fat and total fatty acids in blood and tissues, in which the free acids are converted into their potassium salts and the unsaponifiable fat is extracted by light petroleum.

In the estimation of lipoid-phosphorus, it is considered that ether is the best solvent for the extraction of the lipoids. W. O. K.

Estimation of Chloral Hydrate. E. RUPP (*Pharm. Zentr.-h.*, 1923, **64**, 151).—In the iodometric estimation of chloral in chloral hydrate it is essential that the iodine solution be added before the alkali solution. Ten c.c. of ·1% chloral hydrate solution are treated with 25 c.c. of $N/10$-iodine solution and 2·5 c.c. of $N/1$-sodium hydroxide solution; after ten minutes, the mixture is acidified and the excess of iodine titrated with thiosulphate solution. W. P. S.

Perchloric Acid as a Micro-chemical Reagent. VIKTOR CORDIER (*Monatsh.*, 1923, **43**, 525—536).—Perchloric acid may be used (cf. Deniges, A., 1917, ii, 345) as a sensitive microchemical reagent for the identification of some compounds (*A*, below). Other compounds (*B*) are less delicately responsive to the reagent. Hydrochloric acid, sulphuric acid, water, alcohol, ethylene glycol, glycerol, and nitrobenzene are the solvents used. The colour, crystalline form, and optical properties of the various precipitates obtained are described.

A.—Trimethylamine, tripropylamine, tri*iso*butylamine, tetramethylammonium (iodide), tetraethylammonium (chloride), tetrapropylammonium (iodide), phenylhydrazine, hexamethylenetetramine, triphenylguanidine, pyridine, quinoline, quinaldine, acridine, cinchonamine, scopolamine, cinchonine, quinine, cocaine, veratrine, and guanine.

B.—Ethylenediamine, hydrazine, semicarbazide, aniline, dimethyl *p*-phenylenediamine, tribenzylamine, guanidine, *o*-phenylenediguanide, xanthine, piperine, codeine, sparteine, strychnine, and brucine.

The following compounds do not give crystalline perchlorates: Triamylamine, triethylamine, nitrophenylhydrazine, aminoguanidine, diphenylguanidine, benzyldiguanide, *p*-tolyldiguanide, creatine, diphenylamine, diphenylcarbazide, triphenylcarbinol, nicotine, atropine, berberine, and solanine. E. E. T.

Use of Potassium or Sodium Bromide as a Source of Bromine for Urea Estimations. C. H. Collings (*Chem. News*, 1923, **126**, 180, 181).—A simple apparatus is described in which potassium or sodium bromide solution is decomposed by the gradual addition of nitric acid and the liberated bromine is removed by a current of air and conducted through sodium hydroxide solution, in which it is absorbed to form sodium hypobromite solution for use in the estimation of urea. W. P. S.

Estimation of Carbamide by Hypobromite. B. M. Margosches and Heinrich Rose (*Biochem. Z.*, 1923, **136**, 119—127). —Carbamide and ammonia compounds can be estimated by an alkalimetric hypobromite method. The carbamide (0·2 g.) is treated with 50 c.c. of *N*/10-hypobromite and heated for three minutes at 100°, then treated with 0·2 to 0·3 g. of sodium bromide and 50 c.c. of hydrochloric acid (>*N*/5). The bromine is driven off by gentle heating, and after cooling the excess of acid is titrated with *N*/5-alkali, using methyl-red as indicator. Parallel blank experiments using sodium bromide are an essential feature. H. K.

Reaction of Allantoin Applicable to its Estimation. J. More (*J. Pharm. Chim.*, 1923, **27**, 209—214).—When a solution containing allantoin is treated with Nessler reagent, a yellow coloration is produced and mercurous salts are precipitated; other ureides and ammonium salts yield a precipitate with the reagent, but in this case the precipitate is soluble in dilute hydrochloric acid. For the estimation of allantoin, a solution of the substance in dilute sodium hydroxide solution is treated with an excess of Nessler reagent and, after twelve hours, the mixture is acidified with hydrochloric acid and treated with a known quantity (an excess) of *N*/10-iodine solution. The excess of iodine is titrated subsequently with thiosulphate solution. Two atoms of iodine are equivalent to one molecule of allantoin. The result obtained must be multiplied by 1·08, since only 92% of the allantoin is oxidised. W. P. S.

General and Physical Chemistry.

Refractive Indices of Solutions of Hydrochloric Acid, Acetic Acid, and Ethyl Alcohol in Water at 25° and 30°. HOWARD M. ELSEY and GEORGE L. LYNN (*J. Physical Chem.*, 1923, **27**, 342—345).—The refractive indices of aqueous solutions of hydrochloric acid, acetic acid, and ethyl alcohol have been measured at 25° and 30° for sodium light, using a dipping refractometer. The values of n_D are recorded in tables in the original. J. F. S.

The Atomic Refraction of Mercury. M. TIFFENEAU and CH. SOMMAIRE (*Bull. Soc. chim.*, 1923, [iv], **33**, 293—296).—The atomic refraction of mercury was determined from observations of the refraction of four mercury alkyl compounds, their molecular refractions being calculated from the formula of Lorentz. The following values were obtained: mercury diethyl has n_D^{20} 1·504, d^{20} 2·4268, molecular refraction 33·39, whence, deducting 20·672 for 4C and 10H, the atomic refraction of mercury is 12·718. Mercury di-*n*-propyl has n_D^{22} 1·5138, d^{22} 2·0111, molecular refraction 42·79, whence the atomic refraction of mercury equals 12·882. Mercury di*iso*propyl has $n_D^{23·5}$ 1·52825, $d^{23·5}$ 2·0103, molecular refraction 43·82, and atomic refraction of mercury equals 13·91. Mercury di-*n*-butyl has n_D^{21} 1·5059, d^{21} 1·790, molecular refraction 52·09, and atomic refraction of mercury 12·946. The mean value derived from the unbranched chain compounds is therefore 12·848. The atomic refractions of mercury and the compounds increase as the chain lengthens, and also the introduction of the secondary radicle causes a notable exaltation. These results are in accordance with those previously obtained for lead. G. F. M.

The Molecular Refractions of Chloro-, Dichloro-, and Chlorobromo-acetates. PAULE LAURE VANDERSTICHELE (T., 1923, **123**, 1225—1229).

[The Graphitic Conception of Aromatic Carbon.] A. L. VON STEIGER (*Ber.*, 1923, **56**, [*B*], 998).—In consequence of an error, the value $n_D^{90·35}$ 1·58932 instead of 1·59480 was cited for the index of refraction of anthracene dissolved in naphthalene (A., 1922, ii, 616). The recalculated value for the molecular refraction of anthracene is 65·46, which is in good agreement with the measurements of Krollpfeiffer (this vol., ii, 102). H. W.

A Method for the Separation of the Arc and Spark Lines of Emission Spectra. W. WIEN (*Ann. Physik*, 1922, [iv], **69**, 325—334).—In order to distinguish between the arc and spark lines of a number of gases, positive rays were produced in a high vacuum, and the emission of light was examined. By means of a short condenser, the charged atoms were deviated from their path, and the lines due to these, the spark spectrum, separated from the

lines due to the uncharged atoms, the arc spectrum. The Balmer series for hydrogen were shown to be due to the uncharged atoms. On the other hand, the majority of the oxygen lines were deviated; the undeviated lines belong to the series spectrum. For nitrogen, the relationships are more complex, but the arc and spark spectra are found to agree with Stark's classification. The negative band spectrum was found to be given by positively charged molecules, and the positive band spectra from the uncharged molecules. The mercury lines observed were due to uncharged atoms. W. E. G.

Spark Spectra of Higher Order. LÉON BLOCH and EUGÈNE BLOCH (*Compt. rend.*, 1923, **176**, 1062—1063).—The authors claim priority over Dunoyer for the method of resolving a spark spectrum into several spectra of different categories, and for the application of the method to the case of mercury (cf. *ibid.*, 1910, **153**, 833, 933).
G. F. M.

Arc Spectra and Ionisation Potentials in Dissociated Gases. K. T. COMPTON (*Proc. Amer. Phil. Soc.*, 1922, **61**, 212—226; cf. A., 1921, ii, 368).—The arc was studied in a new type of discharge tube permitting the use of an atmosphere of atomic hydrogen. Critical potentials were also studied by a modification of Lenard's method. For hydrogen, six critical potentials were observed: 10·1, 12·1, and 13·8 are associated with the atom, the first two being radiation potentials, and the last the ionisation potential. These values correspond respectively with the first and second lines and the convergence frequency of the Lyman series. The values 11·3, 12·8, and 16·2 refer to the molecule, being due, respectively, to ionisation without dissociation, dissociation plus radiation from an atom, and dissociation plus ionisation of an atom. The lowest voltage at which an arc can be maintained in hydrogen is 16·2 volts.

A similar study of nitrogen showed the arcing voltage to be 16·15 volts, at which value the positive bands were observed. One of these increased in intensity with further increase of voltage, and the other decreased. The negative band appeared at above 18 volts, and increased in strength with the voltage. The lines in the visible region of the spectrum were not seen at a potential below 70 volts. Whilst dissociation of nitrogen was impossible at temperatures obtained by the heated tube, dissociation by electronic bombardment was facilitated by electrically heated tungsten.
CHEMICAL ABSTRACTS.

Observations on the Structure of the Hydrogen Lines H_α and H_β. A. E. M. GEDDES (*Proc. Roy. Soc. Edin.*, 1923, **43**, 37—42).—According to Sommerfeld's theory of the fine structure of spectral lines, the separation of the doublets for all members of the Balmer series of hydrogen lines should be constant, and correspond with a value $\delta\nu = 0·365$ cm.$^{-1}$. The author finds for H_α and H_β, respectively, the values $\delta\nu = 0·34$ and $0·33$ cm^{-1}. The result is held to support McLennan's view (A., 1921, ii, 666) that the value of $\delta\nu$ decreases with decrease of wave-length, so that the Balmer series must be regarded as a principal series, and not as a subordinate.
J. S. G. T.

Spectra of Hydrogen, Nitrogen, and Oxygen in the Extreme Ultra-violet. J. J. Hopfield (*Physical Rev.*, 1922, **20**, 573—588; cf. this vol., ii, 1).—Contrary to belief, oxygen and other gases are found not to be opaque in the extreme ultra-violet region, and a method has been developed for their examination. For hydrogen, wave-lengths are given for ninety lines from λ 885·6 to λ 1059·2. The resonance line is superimposed in the fourth order on the H_β line; hence its wave-length is 1215·68 ± 0·03 Å. This coincidence confirms the Bohr formula for this line. In the case of nitrogen, the continuous discharge gives chiefly the band spectrum, nineteen bands from λ 1025·8 to λ 1384·7 being measured; the disruptive discharge gave fifty new lines. It appears probable that Lyman's (*Astrophys. J.*, 1916, **43**, 89) helium lines are really due to air. With the disruptive discharge, oxygen yielded about one hundred new lines, extending to λ 507·2; when mercury vapour was present, about 15 additional lines, extending to λ 433·0, were obtained. A. A. E.

Emission and Absorption of Halogens in the Visible and Ultra-violet Regions. A. L. Narayan and D. Gunnayya (*Phil. Mag.*, 1923, [vi], **45**, 827—830).—The emission spectra of bromine and chlorine are line spectra the nature of which depends on the intensity of the discharge and the temperature of the tube. As the temperature increases, some of the lines are reinforced and others disappear. The absorption spectra have been studied up to 2000 Å. All these vapours give a banded spectrum in the yellowish-green region between 5800 Å. and 5000 Å., and at the same time general absorption begins at the ultra-violet and extends up to 4900 Å. With increase of pressure, the bands become darker and a few more are added at the red end, and the general absorption band extends more and more up to the green, where the banded spectrum begins. The absorption of bromine vapour gradually increases as the temperature rises from 30° to 600°, until at the latter temperature it absorbs almost the whole of the ultra-violet up to 2000 Å.; this is the temperature of maximum absorption. In the case of chlorine, the absorption increases slightly towards the red end with rise in temperature, but towards the short wave-length side there is no appreciable change. The maximum absorption for iodine occurs at 300°. The emission and absorption spectra of the halogens are not complementary. W. E. G.

Structure of the Band Spectrum of Helium. II. W. E. Curtis (*Proc. Roy. Soc.*, 1923, [*A*], **103**, 315—333).—In continuation of previous work (A., 1922, ii, 330), the author has investigated the structure of seven doublet bands, near λλ 4650, 3680, 3350, 5130, 4000, 3630, and 3460 Å., in the spectrum of helium. Each band consists of three series, two of which proceed to a head, whilst the third does not. Tables of wave-lengths and least square empirical formulæ are given for the constituent series of each band. The structure of the bands is considered in the light of the quantum theory, and it is shown that the doublet

separations should tend to decrease in passing to higher members of the series, but not to vanish, a result which is in accordance with the measurements of Fowler (A., 1916, ii, 118). Kratzer's half-quantum hypothesis (A., 1922, ii, 409) is applied to discuss the displacement of the more refrangible branches of the bands. A graphical method of calculating moments of inertia of the molecules concerned in the emission of the spectrum is detailed, and numerical values of the initial and final moment are calculated in the case of each of the bands. Initial values so calculated range from $2 \cdot 00 \times 10^{-40}$ to $2 \cdot 17 \times 10^{-40}$ whilst final values range from $1 \cdot 71 \times 10^{-40}$ to $1 \cdot 76 \times 10^{-40}$. The differences between the stable and energised moments of inertia are large compared with the variation of the latter among themselves, and indicate that whilst the removal of the electron from the innermost to the next orbit considerably modifies the configuration of the molecule, subsequent transitions have relatively little effect. No perturbations were found in the bands λλ 6400, 4546, and 5730, previously studied, but in the main series of doublets, λλ 4650, 3680, and 3350, five cases occur. These displacements (obs.-calc.) range from $-2 \cdot 11$ to $+1 \cdot 50$ cm.$^{-1}$. They originate in disturbances of the initial energised state of the molecule. Their complete explanation requires possibly the postulation of an additional molecular type in addition to the whole- and half-quantum types. A new combination law in the form $R'(m)-P(m+1)$=constant, is shown to hold for bands of the same series and for the same value of m. J. S. G. T.

Series Spectra the Emission of which is Associated with more than One Electron. GREGOR WENTZEL (*Physikal. Z.*, 1923, 24, 104—109).—Certain lines in the neon spectrum are produced in pairs by the simultaneous transference of two electrons, one from the 2_2 to an outer orbit, and the other from 2_1 to 2_2. The energy changes involved in these passages are discussed with the aid of a diagram and it is shown that the difference between the work of excitation for two such lines, will be nearly the same as the work involved in the transference of an electron from L_1 to L_2 which gives rise to a line in the Röntgen spectra. The Ritzsche term (A_1A_1') may be derived from the Ritzsche formula, but to obtain the non-Ritzsche term (A_2A_2') a constant amount 782 cm.$^{-1}$ must be added. The spectra of calcium, barium, and strontium are studied from this point of view, and values for the term differences, the ionisation work I_2-I_1, and the work of excitation A_2-A_1, are given for a number of lines. W. E. G.

Regularities in the Red Xenon Spectrum. L. A. SOMMER (*Z. Physik*, 1923, **13**, 85—93).—This work was undertaken in order that a comparison might be possible between the spectrum of xenon and that of ionised cæsium. The measurements of Baly, Merrill, and Meggers have been employed. In all, 148 lines have been arranged in pairs and groups on the basis of constant frequency differences. The intensities, λ and $\gamma_{vac.}$ are given. The comparison with the cæsium spectrum will shortly be communicated.

W. E. G.

The Mass Spectra of the Chemical Elements. IV. F. W. ASTON (*Phil. Mag.*, 1923, [vi], **45**, 934—954; cf. A., 1921, ii, 474). —The photographic plates used in this investigation have been improved by a process of Schumannisation, consisting in partly dissolving away the gelatin from the plate by means of sulphuric acid. The doubly-charged helium atom was sought for without success. The isotopes of nickel were investigated by employing nickel carbonyl diluted by carbon dioxide, and the atomic weights of its isotopes were 58 and 60, respectively. The intensity relation between the lines agrees with that predicted from the experimental atomic weight. The isotopes of titanium and chromium could not be determined when the chlorides were employed on account of the action of the chlorine atoms on the material composing the apparatus. Also lead ethyl and zinc methyl gave unsatisfactory results. The two weak xenon lines, 128, 130, previously suspected, have been confirmed, and two new components at 124 and 126 discovered after considerable over-exposure of the plate. Tin in the form of tin tetramethyl gave the isotopes 116, 117, 118, 119, 120, (121), 122, and 124; the values are less than whole numbers by 2—3 parts in 1000, as was detected by an examination of the line $Sn^{120}CH_3$, which is asymmetrically situated with respect to the two xenon lines, 134, 136. Only one iron line could be definitely identified, and this differed slightly from the whole number rule. Cadmium lines could not be obtained when the metal was volatilised inside the discharge tube, but its introduction led to the complete removal of the mercury lines. On volatilisation, selenium gave five strong lines, 76, 77, 78, 80, 82, and a faint sixth at 74, and these were confirmed by the occurrence of lines due to CSe, COSe, and CSe_2. Three are isobaric with three of the krypton lines. No success was obtained with tellurium or beryllium. Aluminium appears to be a simple element, and no isotope of chlorine occurs at 39. Trimethylstibine gave two strong lines at 121, 123, the former being slightly the more intense, and these lines showed no appreciable deviation from the whole number rule. A complete list of the known isotopes is given. W. E. G.

The Relationship between the Arc Spectrum of Sodium, the First Spark Spectrum of Magnesium, and the Second Spark Spectrum of Aluminium. E. FUES (*Z. Physik*, 1923, **13**, 211—220).—In a previous paper (cf. this vol., ii, 1, 103), it was shown how the terms in the arc spectrum of sodium could be utilised to determine the potential function in the inner field of the atom. It is now possible to extend these deductions from Na^{I} to the related spectra, Mg^{II}, and Al^{III}, although the configurations of these three systems are not exactly identical. For the calculation of the corresponding magnesium and aluminium spectra, only the data for Na^{I} and the value of the L_1 term of magnesium and aluminium are needed. The deviations between the experimental and calculated values, which increase with increasing atomic number, do not disturb the high degree of relationship between the three spectra. W. E. G.

Wave-length Measurements in the Arc Spectra of Neodymium and Samarium. C. C. KIESS (*U.S. Bur. Standards Sci. Papers*, 1922, **18**, 201—219; cf. A., 1922, ii, 244).—The arc spectrum of neodymium has been investigated between λ 5474·72 and 8935·97, and that of samarium between λ 5475·20 and 9264·59, involving about 1500 lines in each, of which 130 are common to both. The latter are of unknown origin, and may possibly be characteristic of the intermediate unknown element of atomic number 61.

A. A. E.

Series-spectra of the Aluminium Sub-group. J. A. CARROLL (*Proc. Roy. Soc.*, 1923, [*A*], **103**, 334—338).—The author has investigated the absorption spectrum of thallium vapour at a temperature of 500—600°, over the range λλ 7000—2500 Å. No trace of absorption lines corresponding with the principal series was observed. Lines corresponding with the sharp series were observed at λλ 5350·46, 3775·72, 3229·75, and 2580·14 Å., and to the diffuse series at λλ 3529·43, 3519·24, 2767·87, 2921·52, and 2918·32 Å. The line λ 2768 Å. showed absorption on the red side only. The absence of the principal series of lines and the reversal of the subordinate series indicate that, in accordance with the latest developments of Bohr's theory, the normal state of the atoms in the aluminium sub-group of elements corresponds with a 1π orbit and not with a 1σ orbit as in the alkali metals. Of the three outermost electrons in the case of thallium, two are in 6_1 orbits and one in a 6_2 orbit, the latter giving rise to the arc spectrum.

J. S. G. T.

The Spark Spectrum of Gallium in Air and in Hydrogen. ELIAS KLEIN (*Astrophys. J.*, 1923, **111**, 373—379).—The wave-lengths of eighty-three lines, fourteen being questionable and forty-eight new, in the spark spectrum of gallium, between λ 2177 and λ 6414, in air and hydrogen have been measured with an accuracy of about ±0·05 Å. It was found that in air, oxidation takes place, the gallium oxide formed superficially then radiating only the strongest lines of the metal, whilst in the case of nitrogen the bands masked the fainter gallium lines. A. A. E.

The Electric Furnace Spectrum of Iron in the Ultra-violet, with Supplementary Data for the Blue and Violet. ARTHUR S. KING (*Astrophys. J.*, 1922, 56, 318—339; cf. *ibid.*, 1913, **37**, 239). —Previous tables (λ 3884 to λ 7208) are extended to λ 2298. Furnace emission spectra extend into the ultra-violet only as far as the continuous spectrum of a black body at the same temperature, but by using a gas-filled tungsten lamp or by explosion of a series of fine wires, absorption spectra corresponding with either low or high temperatures of the vapour may be obtained extending to λ 2298 or beyond. Tables are given containing the temperature classification of 904 lines in the arc, and in low (1600°), medium (2000°), and high (2300°) temperature furnace spectra; a revised classification of 262 lines, λ 3884 to λ 4531 and a list of the most persistent low temperature lines are also given. Experiments with various metals indicate a parallelism between the

successive temperature excitation stages and the radiation stages as the potential is increased in low voltage vacuum arcs. The furnace method is suitable for the classification of spectra of substances of high b. p. A. A. E.

Behaviour of Spectral Lines at the Positive Pole of the Metallic Arc. Paul W. Merrill (*Astrophys. J.*, 1922, **56**, 475—482).—By using the Pfund type of arc, it was found possible to classify five hundred iron lines between λ 3849 and λ 5763 into six classes according to the degree of increase of the intensity of the lines at the boundary of the small region of luminous vapour just above the point where the core of the arc enters the molten bead which forms the positive electrode. Fair correlation was obtained with King's furnace classification. Similar relationships were found in the case of one hundred and eighty cobalt lines and some nickel lines. A. A. E.

An Explanation of Complicated Spectra (Manganese, Chromium, etc.) by the Inner Quantum Number. A. Sommerfeld (*Ann. Physik*, 1923, [iv], **70**, 32—62).—The conception of the inner quantum number has been further extended (cf. *ibid.*, 1920, **63**, 221) to provide an explanation of complicated line spectra. The choice of the combinations between the three quantum numbers k, n, and j is limited to the following: for the inner quantum number, $j \rightarrow \begin{cases} j-1 \\ j \\ j+1 \end{cases}$ and for the "azimutal" quantum number, $k \rightarrow k \pm 1$. The Landé condition that the combination $O \rightarrow O$ is impossible may be used to determine the absolute values of the quantum numbers. With the aid of the conception of the inner quantum number, it is possible to predict the intensities of the spectrum lines, those lines being the strongest in which j changes by the same amount as k; the intensity becomes weaker the more the change of Δj deviates from the change Δk. These rules are applied to the members of the line spectra of manganese and chromium. For chromium, the passage $O - O$ is absent and the existing lines are in agreement with the above principles, but in the scheme formulated for manganese the combination $O - O$ is present, and doubt arises as to the absolute values for the quantum numbers. The number of levels into which the S, P, D, . . . series or s, p, d, . . . series are divided increases according to the numbers 1, 3, 5 . . . The relationship between the inner quantum number and the impulse moment, and between the latter and the magneton number, is discussed. Doubt is expressed as to whether the paramagnetic moment is identical with the impulse moment derived from the inner quantum number. W. E. G.

Series Relationships in the Arc Spectrum of Chromium. H. Gieseler (*Ann. Physik*, 1922, [iv], **69**, 147—160).—From the observed Zeeman effect and with the aid of the Landé theory (*Z. Physik*, 1921, **5**, 231), it has been possible to arrange and classify the arc spectrum of chromium. The key to the chromium spectrum

is given by the $3a/2$-groups which had been already discovered for calcium, barium, and strontium. In the arc spectrum of chromium, three such groups occur, which consist of 12 lines. These are arranged in Rydberg schemes, giving the intensity λ_{air} in Å., $\nu=10^8\lambda^{-1}_{vac.}$, and the differences between related lines. Also two *pd* series have been found, consisting of twelve lines, and from the Landé theory the separation factor g for the d terms has been calculated. The agreement between theory and experiment is good. The p differences also occur in combination with s terms in one series, and a second, somewhat faint group possibly with s term differences has been discovered, but it was not possible in this group to measure the Zeeman effect. A table is given of the Zeeman effect for lines in the chromium spectrum. W. E. G.

Spectral Series and Ionisation and Resonance Potentials of Chromium and Molybdenum. M. A. Catalan (*Compt. rend.*, 1923, **176**, 1063—1065).—One system of series of triplets of the arc spectrum of molybdenum has already been given (this vol., ii, 105) and a second parallel series is now tabulated. The diffuse term is also quintuple and the diffuse triplets are formed by nine components. By means of the terms $1s$ of chromium and molybdenum (54640·9 and 57420·4) the ionisation potentials of these elements are found to be 6·7 and 7·1 volts, respectively. The first resonance potentials calculated from the triplets λ 4254, 4275, 4290, and λ 3798, 3864, 3902 are 2·89 and 3·19 volts from chromium and molybdenum, respectively. G. F. M.

The Existence of New Lines, including a Sommerfeld Doublet, excluded by the Principle of Selection in the *L*-series of the Heavy Elements. Pierre Auger and A. Dauvillier (*Compt. rend.*, 1923, **176**, 1297—1298).—A record of observations of new lines in the *X*-ray spectra of certain heavy elements. They correspond with the combinations M_4L_1 and M_5L_1, the former forming a Sommerfeld doublet with the β_{11} line. Details are also given of twenty-five L lines in the spectrum of tantalum and of 4 K lines in that of ruthenium. H. J. E.

An Extension of the Fundamental Ultra-red Absorption Band of Hydrogen Chloride. W. F. Colby, C. F. Meyer, and D. W. Bronk (*Astrophys. J.*, 1923, **57**, 7—19).—The fundamental absorption band of hydrogen chloride at 3·4 μ has been further studied (cf. A., 1922, ii, 5) and extended from 3·9 to 4·2 μ by the aid of a grating having 2,800 lines to the inch. Seven new principal lines have been measured, and a series of faint lines has been discovered between the principal lines in the region $m = -12$ to $m = -17$. The possibility of these faint lines being Rowland ghosts, Lyman ghosts, or secondary reflections is discussed and rejected. They are observed only when the gas is heated at about 500°. A table and a diagram of the thirty-nine lines of the entire known spectrum of hydrogen chloride are given, and revised constants have been computed for Kratzer's theoretical formula.

A. A. E.

The Effect of certain Dissolved Substances on the Ultra-red Absorption of Water. J. R. COLLINS (*Physical Rev.*, 1922, 20, 486—498).—In a study of the absorption of water from 0·8 to 2·3 μ, the wave-lengths of maximum absorption were found to be 0·97, 1·20, 1·44, and 2·00 μ, the corresponding coefficients of absorption being 0·448, 1·220, 29·4, and 103, respectively. In the absorption spectrum of water vapour, the bands at 1·44 and 2·00 μ are stronger, and the other two bands weaker than for liquid water; it is suggested that the former and the latter bands are associated with different kinds of molecules. The ultra-red absorption spectra of aqueous solutions of the following substances from 0·8 to 2·3 μ have been determined: sodium, potassium, and lithium hydroxides; aluminium, calcium, magnesium, sodium, and strontium chlorides; silver, aluminium, magnesium, ammonium, and zinc nitrates; aluminium and zinc sulphates; sodium thiosulphate. In all cases, the solutes decreased the absorption in the water band at 1·44 μ and probably also in that at 2·00 μ, whereas all except aluminium and zinc sulphates and the hydroxides increased the absorption in the bands at 0·97 and 1·20 μ. The results do not agree with the solvate theory which ascribes the effect to the formation of hydrates.

A. A. E.

Absorption of Potassium Vapour. A. L. NARRAYAN and D. GUNNAYYA (*Phil. Mag.*, 1923, [vi], 45, 831—834; cf. A., 1922, ii, 679).—The absorption spectrum of potassium vapour has been studied at high vapour densities up to 950° with the view of extending the Balmer series for this element. Between 750° and 800°, this series could be observed up to the thirtieth member, and at slightly higher temperatures evidence of the presence of some members of the diffuse series was obtained. In the red-channelled spectrum 15 bands were measured.

W. E. G.

The Fluorescence and Channelled Absorption Spectra of Cæsium and other Alkali Elements. J. C. McLENNAN and D. S. AINSLIE (*Proc. Roy. Soc.*, 1923, [*A*], 103, 304—314).—Experiments are described showing that potassium vapour, in addition to the banded fluorescence and absorption spectra observed by Wood and Carter (*Physical Rev.*, 1908), possesses a closely-banded absorption spectrum in the region of wave-lengths λ 8625—8200 Å., longer than that of the first member, λ 7699·01 Å., of its doublet series, and also a more widely spaced one in the region, λ 4500—4150 Å., of the second member of the series. The channelled absorption spectrum of rubidium was shown to consist of at least seventeen bands, four additional to those observed by Carter (A., 1910, ii, 672) and to extend from λ 6700 Å. to λ 7100 Å. The fluorescence spectrum of rubidium was found to consist of a wide band between λ 6540 Å. and λ 7100 Å. It was channelled on the long wave-length side, but continuous on the side of shorter wave-lengths. With cæsium vapour, a channelled absorption spectrum consisting of bands at $\lambda\lambda$ 7585, 7659, 7706, 7749, and 7778 Å., was found, and a fluorescence spectrum consisting of an unresolved band extending from about λ 7540 Å. to λ 8000 Å. Lithium probably possesses

a banded absorption spectrum in the ultra-violet. It is considered very probable that the complete fluorescence and channelled absorption spectra of cæsium and rubidium have the same characteristics as the corresponding spectra of sodium and potassium. J. S. G. T.

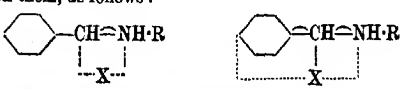
Rare Earths. XIII. Absorption Spectra. L. F. YNTEMA (*J. Amer. Chem. Soc.*, 1923, **45**, 907—915).—The absorption spectra of solutions of chlorides of praseodymium, neodymium, samarium, dysprosium, holmium, erbium, and thulium in the visible region have been measured at various concentrations and thicknesses of solution. Absorption curves have been drawn and the last appearance of each band on dilution has been tabulated. In the case of praseodymium, five bands are recorded with maxima at λλ 4441, 4690, 4891, 5890, and 5974 Å.; with neodymium twenty-two bands were photographed with maxima at λλ 3803, 4185, 4273, 4331, 4612, 4691, 4755, 4803, 5091, 5123, 5205, 5222, 5319, 5726, 5748, 5782, 6228, 6251, 6286, 6374, 6786, and 6877 Å., and in addition faint bands were observed by visual methods at 4293, 4869, 5253, 5731, 5816, 5823, 5888, and 6720 Å. The band 5816 is stated by Baxter and Chapin to occur only in nitrate solutions, and the band 5470, which also occurs in nitrate solutions, was not observed in the present work (A., 1911, ii, 285). With samarium, bands were photographed with maxima at λλ 3740, 3905, 4013, 4071, 4154, 4177, 4411, 4636, 4794, 4893, 4995, 5297, and 5594 Å., and faint bands were also found by visual methods at λλ 4509, 4744, 5277, and 5572 Å. Seven bands were photographed with dysprosium, the maxima lying at λλ 3800, 3873, 3990, 4275, 4502, 4534, and 4754 Å., and a faint band found visually at λ 4778 Å. Twenty-two bands are recorded for holmium, the maxima lying at λλ 3865, 4159, 4174, 4192, 4220, 4273, 4505, 4522, 4549, 4678, 4735, 4799, 4831, 4853, 4910, 5365, 5435, 5493, 6405, 6433, 6530, and 6567 Å. Nineteen bands were photographed for erbium with maxima lying at λλ 4050, 4060, 4072, 4104, 4123, 4422, 4479, 4537, 4555, 4849, 4871, 4913, 5208, 5232, 5416, 5490, 6490, 6526, and 6669 Å., and two faint bands at λλ 5396 and 5515 Å. observed visually. Thulium gives four bands with maxima at λλ 4643, 6588, 6835, and 6999 Å. It is pointed out that the close coincidence of the two holmium bands at λλ 4273 and 4505 Å. with the dysprosium bands at λλ 4275 and 4502 Å. may lead to confusion in the identification of either element in the presence of the other. A method for the quantitative estimation of the rare earths is outlined, which consists in diluting the mixture until the most persistent band has disappeared and taking the ratio between the equivalent thickness of the last appearance in the mixture and in the pure salt. There appears to be no definite periodic arrangement of the absorption bands. J. F. S.

Production of Narrow and Broad Bands in the Absorption Spectra of Substances in Solution and in the Vapour State. VICTOR HENRI (*Compt. rend.*, 1923, **176**, 1142—1145).—From a comparative study of a large number of organic compounds, the following general rules were deduced. A substance having only a single double bond in its molecule, *e.g.*, C=C, C=O, C=N,

or N=O, has only broad bands in its absorption spectrum both in solution and in the state of vapour. A substance with a single molecule containing two or more double bonds either adjacent or conjugated presents numerous narrow bands both in solution or as vapour, distributed in series conforming with the theory of quanta. If the two double bonds in molecules of this type are separated by the introduction of CH_2- groups, the narrow bands fuse together, and only broad bands appear in the spectrum. If the molecule is weighted by the introduction of more and more complicated atomic groups, the narrow bands are widened, and eventually form themselves into broad, continuous bands. Examples of these changes are given in acraldehyde, crotonaldehyde, and mesityl oxide, mono- and di-substitution products of benzene, etc. The mechanism of the production of these bands is discussed, and it is concluded that for molecules containing only a single double bond the first postulate of Bohr does not apply, and only the second is valid, whilst for molecules with two neighbouring double bonds both postulates apply, the first being determined by the existence of an electric polarity in the molecule. G. F. M.

The Ultra-violet Absorption Spectrum of Chlorobenzene Vapour. Determination of the Molecular Structure. VICTOR HENRI (*Compt. rend.*, 1923, **176**, 1298—1301).—A more complete study of the absorption spectrum resulted in the measurement of more than seven hundred and fifty bands between 2755 and 2262 Å., the greater number of these being observed at a pressure of 3 mm. The spectrum consists of eight groups of bands each of which is made up of several series. The conclusion is drawn that the molecule has two separate moments of inertia in relation to two axes of rotation; one of these corresponds with that of benzene and is about an axis passing through the CCl-group and the CH-group in the para-position with respect to it, the other is smaller and perpendicular to this. The molecule is regarded as a flattened octahedron, the centre of gravity of the CCl-group being half the distance of that of the opposite CH-group from the median plane. H. J. E.

Relation between Absorption and Structure. IV. Structure and the Absorption of Light of Acid Additive Products of Benzylideneimines. V. A. IZMAILSKI (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 167—189; cf. A., 1915, ii, 198; 1916, i, 287).—The absorption spectra of different acid salts of various substituted benzylideneanils are measured, and the structure of these salts discussed from these data. In view of the fact that many of these salts can exist in two chromoisomeric forms, so-called meso-formulæ are given them, as follows:



where X is an acidic radicle and the broken lines represent partial valency linkings. Those substances in which the para-position in the aldehydic benzene ring is occupied by atoms or groups more

unsaturated with regard to valency than the corresponding carbon atom, as, for example, the amino- and dimethylamino-groups, exhibit more strongly marked tendencies to exist in forms represented by the two meso-formulæ shown above. Absorption of light by organic substances is concluded to be due, not to any particular group or radicle of the molecule, but to be a function of the molecule as a whole, as is shown by the very similar absorption constants obtained for *p*-dimethylaminobenzylideneanil, $NMe_2\cdot C_6H_4\cdot CH:NPh$, and benzylidene-*p*-dimethylaminoanil, $CHPh:N\cdot C_6H_4\cdot NMe_2$. Absorption curves are drawn for the following substances: Benzylideneanil, its sulphate, and its hydriodide, which exists in two forms; for diphenylmethylidenephenylimine, $Ph_2C:NPh$, its hydriodide and hydrobromide; for *p*-dimethylaminobenzylideneanil, its hydrobromide, dihydrobromide, acetate, and diacetate, and for benzylidene-*p*-dimethylaminoanil. R. T.

The Absorption Spectra of Vegetable Dyes of the Flavone Series. I. YUJI SHIBATA and KENSHÔ KIMOTSUKI (*Acta Phytochim.*, 1923, **1**, 91—104).—The vegetable colouring matters of the flavone series show two characteristic absorption curves in the ultra-violet, and since the position of these bands is affected by the number and orientation of the hydroxyl groups, the ultra-violet absorption spectra serve as a ready means of identifying the different members of the series. The observations are best made in 1/10,000 molar alcoholic solution. Flavone itself has the two bands at frequencies 3500 and 4050. The position of the second band is scarcely influenced by hydroxyl groups, but the first is shifted towards the red by hydroxyl groups in the benzopyrone nucleus, and in the opposite direction by hydroxyl in the side phenyl group. Moreover, the depth of this band increases with the number of hydroxyl groups, as in the series kaempferol, quercetin, myricetin, containing, respectively, one, two, and three hydroxyls in the side phenyl group. Acetylation neutralises the influence of the hydroxyl groups, and diacetylchrysin and penta-acetylquercetin have exactly the same absorption spectrum as flavone.

In chrysin, apigenin, and luteolin, the head of the first absorption band is near 3500; chrysin is exceptional in that the second band is also shifted considerably towards the red. Galangin, kaempferol, and kaempferide form a closely-related group with the first band at 2650. In quercetin, *iso*rhamnetin, and myricetin, this band is also at 2650 but is deeper.

The absorption bands of the flavone colouring matters from seventeen different plants were examined, and by comparison of the curves obtained with those of the above substances it was possible to determine to what type the unknown substances belonged. Exact correspondence was not obtained, probably on account of impurities in the plant preparations. E. H. R.

Absorption Spectra of Pyrrole and its Derivatives. I. The Absorption Spectrum of Pyrrole. T. V. KORSHUN and KLARA VLADIMIROVA ROLL (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 153—156).—The absorption spectrum of pyrrole is found to contain

two bands, occurring at $1/\lambda$ 3200—3500, and $1/\gamma$ 3750—4000, these positions being close to those found for pyrrole derivatives at concentrations more than a thousand times smaller. These bands were not observed by Hartley and Dobbie (T., 1897, **73**, 603), who used weaker solutions, or by Purvis (T., 1910, **97**, 1657), who did not take readings of the part of the curve corresponding with the second band. The existence of these bands confirms Valiaschko's law (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1820), that the absorption spectra of cyclic substances are essentially a feature of the nucleus, and that substitution merely intensifies and modifies them. R. T.

The Low-voltage Arc in Mercury Vapour and its Relation to Fluorescence. Y. T. Yao (*Physical Rev.*, 1923, [ii], **21**, 1—21).—The effect of initial emission velocities of electrons on minimum ionising potentials is examined, and a proof of the fundamental importance of the critical point of 4·9 volts for mercury vapour is held to have been obtained. Low voltage arc phenomena were studied under identical conditions for the two cases, (*a*) when the vapour was very near to the liquid surface, and (*b*) when it was far removed from it. The difference (about 1·2 volts) in the minimum voltage for maintenance of the arc, together with the known dependence of fluorescence on the continuance of distillation of mercury, demonstrate the close relation existing between the production of arcs and the excitation of fluorescence and resonance radiation in mercury vapour. It is suggested that there may be some influence, due either to the arrangement of internal electrons or to the influence of neighbouring molecules, which increases the probability of ionisation along the $1S-mp_2$ path as compared with the $1S-mP$ path in freshly distilled vapour, but that this influence does not appreciably affect the potential energy of the electron in the $1S$ state. A. A. E.

Phosphorescence Caused by Active Nitrogen. E. P. Lewis (*Nature*, 1923, **111**, 599—600).—Active nitrogen excites a green or bluish-green phosphorescence in a number of solid substances; the spectra are nearly all continuous. A strong effect is produced with uranium nitrate, uranium ammonium fluoride, zinc sulphide, barium chloride, strontium chloride, calcium chloride, and cæsium chloride, whereas a weak effect is given by lithium chloride, sodium chloride, potassium chloride, sodium iodide, potassium iodide, sodium carbonate, and strontium bromide. The phenomenon may be due to chemical reaction with the active nitrogen, or to the presence of free electrons. A possible reason for the afterglow is briefly discussed, it being suggested that if there is enough oxygen present to remove most, but not all, of the electrons, recombination may proceed slowly, the spectrum of the afterglow being due to the recombination of electrons with positive molecular ions. A. A. E.

The Establishment of Einstein's Equivalence Law, and its Significance in Photochemical and Chemical Processes. Fritz Weigert (*Z. Physik*, 1923, **14**, 383—409).—Einstein's

thermodynamic deduction of the photochemical equivalence law is based on the conception of an ideal perfectly reversible photochemical reaction, and leads to the relation $Q=Nh\nu$ between the heat tone, Q, of the reaction and the number of quanta N absorbed in the reaction. It is shown that a stable photochemical equilibrium is a physical impossibility. Einstein's expression for the velocity of a photochemical reaction may be quantised only when component reactions of a non-photochemical nature are eliminated from consideration in the complete reaction. Under these conditions, the equivalence law for the primary photochemical reaction is expressed in the form $q=Nh\nu$, q being the energy absorbed in the primary process. Alternatively, the law may be expressed in the form $q=\Sigma nh\nu$, where $N=\Sigma n$. The mode of deduction of the result does not differentiate between equilibrium in a photochemical or thermodynamic system, and it is concluded, therefore, that N energy quanta are absorbed in any molecular chemical or photochemical process. The fundamental equation $u_{\nu T}=8\pi h\nu^3 . e^{-Nh\nu/RT} . /c^3$ of the radiation hypothesis is deduced, and it is pointed out that the correlation by Arrhenius and others of the activating energy q with the thermochemical and optical properties of the system is not in agreement with the completely non-specific nature of the equation $q=Nh\nu$. The primary process in all chemical processes is conceived as consisting of the ejection of an electron from a quantised orbit accompanied by quanta of energy. Experiments indicate that absorption of radiation occurs in such a case only when the electron does not return to its original orbit, but enters a higher quantised orbit or becomes attached to another particle. J. S. G. T.

Photo-chemistry of Potassium Permanganate. I. Application of the Potentiometer to the Study of Photochemical Change. E. K. Rideal and R. G. W. Norrish (*Proc. Roy. Soc.*, 1923, [*A*], **103**, 342—366).—Potassium permanganate solutions, when illuminated by ultra-violet light, undergo a marked change of electrode potential, which reverts slowly to its original value when the light is extinguished. The authors show that this change is due to an alteration in the hydrogen-ion concentration of the solution brought about by photochemical decomposition of the potassium permanganate, thus: $2KMnO_4=K_2O,2MnO_2+3O$. The compound $K_2O,2MnO_2$ is precipitated and a red sol of manganese dioxide and potassium manganite is formed. The decomposition is unimolecular over the range of concentration studied, and it is shown how the velocity constant can be calculated either from the changes of electrode potential during illumination or from the dark-recovery curve. Values of K determined by either of these methods are in very close agreement with the results of a spectrophotometric determination ($K=0{\cdot}00149$). A photochemical stationary state is produced in the solution owing to removal of potassium hydroxide by combination with hydrated manganese dioxide. The rate of decomposition of potassium permanganate is increased by the addition of sulphuric acid to the solution. In such solutions,

the reaction, throughout almost the whole of its course, is of zero order, the constant velocity indicating continuous complete absorption of the photoactive radiation. This change in the type of decomposition is connected with the non-formation of colloid in the acid solution. Ammonium nitrate, uranyl nitrate, and potassium hypochlorite solutions afford photoactive effects similar to those observed with potassium permanganate. A photolytic cell containing potassium permanganate and yielding an *E.M.F.* equal to 0·215 volt is described. J. S. G. T.

The Photochemistry of Unstable Substances. EDMUND JOHN BOWEN (T., 1923, **123**, 1199—1206).

The Applications of Photography to Chemistry. PIERRE JOLIBOIS (*Bull. Soc. chim.*, 1923, [iv], **33**, 229—245).—A lecture delivered before the Strasbourg-Mulhouse section of the Société Chimique de France. G. F. M.

Variation of the Photoelectric Activity of a Potassium Ferrocyanide Solution with Concentration. J. H. J. POOLE (*Phil. Mag.*, 1923, [vi], **45**, 895—906).—The effect of changes in the concentration of ferrocyanide solutions has been studied with the view of throwing light on the possible source of the photoelectron. The activity of the solution increases in a linear manner with increase in concentration, but at the higher concentrations the activity increases more rapidly than the concentration. This fact favours the view that the undissociated molecule is responsible for the photoelectric properties of the solution. Since potassium ferricyanide was found to be nearly inactive in solution, the effect cannot have been due to the positive ion. When the activity is plotted along the ordinate against the number of undissociated molecules in the solution, a straight line is obtained for the lower concentrations, but the curve bends upwards, as before, for the higher values. Surface concentration effects do not appear to account for the phenomenon. An alternative explanation is suggested, which ascribes the increased photoelectric effect in concentrated solutions to association of the undissociated molecules. This is in agreement with the high photoelectric activity of the solid salt. W. E. G.

Tracks of α-Particles in Helium. D. M. BOSE and S. K. GHOSH (*Nature*, 1923, **111**, 463—464).—Photographs have been obtained of the ionisation tracks of α-particles from polonium in helium. Both electrons are ejected on the same side of the α-particle track. Tracks indicating the collision of an α-particle with an atom more complex than hydrogen or helium may possibly originate from the breaking up of a nitrogen nucleus with the expulsion of a hydrogen nucleus. A. A. E.

The Continuous Röntgen Spectrum. HELMUTH KULENKAMPFF (*Ann. Physik*, 1922, **69**, 548—595).—An investigation into the dependance of the intensities and spectral distribution of the continuous Röntgen rays on the atomic number of the metal forming the anticathode, and on the voltage of the cathode rays.

The Röntgen rays from the eight metals, aluminium, iron, cobalt, nickel, copper, silver, tin, and platinum, have been examined at the constant voltage, 10470 volts, over a wave-length $\lambda=1\cdot0$ to $\lambda=2\cdot8$ Å., and for two metals, silver and platinum, for the voltage interval, 7000 to 12,000 volts. Corrections were made to the observed intensities for the absorption in the aluminium window of the tube and in the adjoining air space, and for the absorption inside the anticathode material. The dependance of the reflecting power of the crystal on the wave-length of the Röntgen rays and the length of the ionisation chamber were also taken into account. The intensity maximum of the Röntgen rays is displaced slightly towards the shorter wave-lengths with increase in atomic weight. The intensity maximum and the total intensity is directly proportional to the atomic number of the element. The measurement of the intensity maxima and the total intensities for iron, cobalt, and nickel are made difficult by the presence of strong spectral lines, and by selective absorption on the short wave-length side of the maximum. When the specific intensity $J\gamma$ is plotted against $\gamma_0-\gamma$, the curves show a linear trend throughout the larger part of their course. The tangent to these curves is directly proportional to the atomic number, and on changing the potential (atomic number constant) a parallel series of curves is obtained. Thus, $J\gamma=\text{const.}\ (\gamma_0-\gamma)$, where the constant is dependent on the atomic number, and not on the potential. In the neighbourhood of the limiting frequency, a striking break in the curve occurs. W. E. G.

Characteristic *L* Absorption of *X*-Rays for Elements of Atomic Numbers 62 to 77. J. M. Cork (*Physical Rev.*, 1923, [ii], **21**, 326—333).—Compounds of samarium (62), gadolinium (64), dysprosium (66), erbium (68), ytterbium (70), tantalum (73), tungsten (74), osmium (76), or iridium (77) were uniformly distributed over a filter-paper and interposed between a Coolidge tube with a tungsten target and a calcite crystal. The emission lines of tungsten were used as reference lines for the measurement of the wave-lengths of the absorption edges. The following are tabulated: (*a*) The *X*-ray spectrum of tungsten, together with a proposed notation, based on the use for each emission line of a symbol designating the initial and final energy levels, *e.g.* $\lambda\,1\cdot0596$, γ_3 (Siegbahn), x (Sommerfeld), is $L_3\gamma_5$. (*b*) The mean values of the observed wave-lengths, with values of ν/N and $\sqrt{\nu/N}$. (*c*) The L_2-L_1 regular doublet frequency differences expressed as $\Delta\nu/N$, exhibiting good agreement with values computed from Sommerfeld's formula, and the frequency differences of the L_β and $L_{\alpha'}$ emission lines. (*d*) The energy levels of the various electronic orbits expressed in terms of ν/N. The expression $\sqrt{\nu/N}$ for L_1, L_2, and L_3 has been plotted as a function of the atomic number, and it is pointed out that the deviation of the curves from Moseley's linear relation may be qualitatively explained by taking into account the nuclear defect due to other electrons and the relativity correction. The observed results are in approximate agreement

with the empirical expression $\Delta(\nu/N)=KZ^5$, where Z is the atomic number, and K has the values $4{\cdot}44\times10^{-8}$ for L_2-L_1, $1{\cdot}97\times10^{-9}$ for M_2-M_1, and $9{\cdot}60\times10^{-9}$ for M_4-M_3. A. A. E.

X-Ray Absorption Coefficients of Carbon, Hydrogen, and Oxygen. A. R. Olson, Elmer Dershem, and H. H. Storch (*Physical Rev.*, 1923, [ii], 21, 30—37).—The work of Aurén (A., 1919, ii, 89), in so far as it appeared to disclose a large discrepancy between the absorption coefficients for non-homogeneous *X*-rays of graphite and carbon in organic combination, would likewise suggest a difference in the case of aromatic and aliphatic carbon; it has therefore been repeated for the cases of water, benzene, toluene, xylene, mesitylene, heptane, and *cyclo*hexanol. The variation with wave-length between 0·35 and 0·98 Å. is in all cases in accordance with the equation $\mu=A+B\lambda^3$, where (for a gram-molecule in a cell of 1 cm.^{2} cross-section) the values for A are 3·5, 15·3, 19·0, 21·7, 24·2, 21·5, and 20·5, respectively, and for B, 44·5, 74·9, 85·3, 98·3, 113·6, 87·3, and 121·0, respectively. The mass absorption coefficients of hydrogen, carbon, and oxygen for *X*-rays of wave-lengths from 0·25 to 0·98 Å. are computed as follows: $\mu_H=0{\cdot}37+0{\cdot}28\lambda^3$; $\mu_C=0{\cdot}18+1{\cdot}01\lambda^3$; $\mu_O=0{\cdot}16+2{\cdot}785\lambda^3$. These results are in direct contradiction to those of Aurén (*loc. cit.*), and constitute a proof of the additive law. The identity of the constants for the group CH_2 when involving carbon in the aliphatic or aromatic condition, or both, lead to the conclusion that the absorption coefficients of aliphatic carbon, aromatic carbon, and graphitic carbon are the same for wave-lengths less than 1 Å.

A. A. E.

Absorption Coefficients for Homogeneous X-Rays. E. G. Taylor (*Physical Rev.*, 1922, 20, 709—714).—The effect of the interposition of a cell containing a known thickness of various liquids before lead slits and a calcite crystal, by means of which only slightly divergent K_α rays from the molybdenum target of a Coolidge tube were reflected into an ionisation chamber, was measured. The following results were obtained for the molecular absorption: pinene, $1{\cdot}209\times10^{-24}$; limonene, $1{\cdot}206\times10^{-24}$; benzene, $0{\cdot}707\times10^{-24}$; toluene, $0{\cdot}834\times10^{-24}$; *iso*propyl alcohol, $0{\cdot}683\times10^{-22}$; methyl propionate, $1{\cdot}089\times10^{-22}$; ethyl acetate, $1{\cdot}099\times10^{-22}$; acetone, $0{\cdot}679\times10^{-22}$; ethyl formate, $0{\cdot}970\times10^{-22}$; trimethylene glycol, $0{\cdot}986\times10^{-22}$. Atomic absorption coefficients for *X*-rays λ 0·715 Å. are computed as follows on the assumption that absorption is an additive atomic property: carbon, $0{\cdot}1134\times10^{-22}$, oxygen, $0{\cdot}304\times10^{-22}$, hydrogen (calculated from hydrocarbons), $0{\cdot}0048\times10^{-22}$. There are, however, indications that the assumption may not be accurately true. Moreover, when the atomic absorption of oxygen is subtracted from the molecular absorption of water, $0{\cdot}322\times10^{-22}$, a value is found for the absorption of hydrogen approximately twice that determined from the hydrocarbons; the cause may possibly lie in a difference in the strength of the bond uniting the hydrogen to the other elements of the

compound. The atomic absorption of aluminium is found to be $2{\cdot}29\times10^{-22}$. A. A. E.

The Adsorption of the -*B* and -*C* Members of the Radium and Thorium Series by Ferric Hydroxide. JOHN ARNOLD CRANSTON and ROBERT HUTTON (T., 1923, **123**, 1318—1324).

Origin of Radioactive Disintegration. S. ROSSELAND (*Nature*, 1923, **111**, 357; cf. Pease, A., 1922, ii, 757).—In view of the fact that the life-periods of the elements at the beginning of the disintegration series are large, it is possible that the nuclei may be intrinsically stable, the radioactivity of these elements being due to the action of an external field of force originating in the surrounding electrons. In the case of rubidium and potassium, radioactivity might be due to an enhanced efficiency of the perturbations due to resonance in the interaction between nuclear and electronic motion. Consideration of the relative order of magnitude of the diameter of the nucleus and the shortest distance from the nucleus attained by electrons does not appear to exclude the possibility that the existence of radioactivity among elements of high atomic number, and the non-existence of elements of atomic number greater than that of uranium, may be connected with some kind of interaction between the nuclear and external electrons. It is suggested that the nucleus as a whole will rotate, and that this rotational frequency may be comparable with some electronic frequency, the case in which the nucleus rotates with an angular momentum of $h/2\pi$ (when the rotational frequency,

$$w=(h/4\pi^2)(1/Ma^2),$$

where M and a are, respectively, the nuclear mass and radius of gyration about the axis of rotation) being specially considered. A. A. E.

Ionisation by Collision in Helium. J. S. TOWNSEND (*Phil. Mag.*, 1923, [vi], **45**, 1071—1079).—The ionisation of argon and helium by the collisions of electrons and positive ions with molecules of the gas was investigated by Gill and Pidduck by measurements of conductivity between parallel plates (cf. A., 1912, ii, 515). It was found that the processes of ionisation follow the same general laws as had been found previously for other gases. These experiments are not in agreement with modern views on the mode of development of currents in monatomic gases, or with the determination of resonance or ionisation potentials by the valve method. The conductivity between parallel plates should change in a well defined series of steps as the potential increases. In experiments, repeating the earlier work, no such effects have been observed. It is shown that the energy required to ionise a molecule of helium is approximately 12 volts, and the sum of the energies of the electron which ionises the molecule and the electron which is set free is 16·6 volts, after the collision. On the other hand, from the valve experiments, ionisation of a molecule of helium takes place on collision with an electron provided the energy of the electron exceeds a minimum value 21 and 25 volts, and it has been con-

cluded that this number of volts represents the loss of energy of an electron when it ionises a molecule. This is not supported by the evidence from the parallel plate experiments. W. E. G.

Thermionic Effects Caused by Alkali Vapours in Vacuum Tubes. IRVING LANGMUIR and K. H. KINGDON (*Science*, 1923, **57**, 58—60).—Metallic cæsium in a vacuum tube forms an adsorbed film consisting of a single layer of atoms completely covering the tungsten filament even at filament temperatures of 600° *K*. or more, the electron affinity of a tungsten surface being greater than that of cæsium-ions (4·52 and 3·90 volts, respectively). The presence of minute traces of certain electro-negative gases increases the tendency of cæsium to be held by such a surface, so that the film then remains intact up to about 900° *K*.; at higher temperatures the film partly evaporates and the electron emission falls rapidly. When a tungsten filament is heated above 1000° *K*. in cæsium vapour at room temperature, the electron emission falls to negligible values, since there is a linear relation between the fraction of the surface covered by cæsium and the logarithm of the saturation current. Cæsium evaporates from the film at 1000° *K*. in the form of neutral atoms, since the electron affinity of a surface partly covered by cæsium may be less than that of a cæsium atom. The measurement of the ion generation may be applied to the accurate determination of the vapour pressures of alkali metals. When a thoriated tungsten filament is used in experiments with cæsium vapour, both the electron emission and the ion generation disappear if the filament is first given a heat treatment by which an adsorbed film of thorium is brought to the surface, the electron affinity of a fully active thoriated filament being only 2·94 volts. Rubidium vapour is similar to cæsium in its effects. A. A. E.

Rate of Evaporation of Electrons from Hot Filaments. WORTH H. RODEBUSH (*J. Amer. Chem. Soc.*, 1923, **45**, 997—998).—In a previous paper (this vol., ii, 303) the author derived an equation from statistical mechanics for the rate of evaporation. This equation had the form $\bar{N}=N\sqrt{RT/E_0\pi}\,.\,e^{-E_0/RT}$, and was tested for the rate of evaporation of electrons from a hot filament by placing $E_0=\varphi$, where φ is the thermionic work function. Further consideration has shown that E_0 should be set equal to $\varphi+2RT$. In the present paper, this has been done, and the equation tested for the cases of tungsten, tantalum, and molybdenum, using data obtained by Langmuir. The calculated value of A is very close to the experimental value. If this equation is generally true, it furnishes a relation between the thermionic work function and the thermoelectric force. The thermionic work function being known, the contact potential between metals can be calculated from the thermoelectric data. J. F. S.

New Evidence regarding the Interpretation of Critical Potentials in Hydrogen. P. S. OLMSTEAD (*Physical Rev.*, 1922, **20**, 613—630).—An experimental separation of the effects due to the atom and those due to the molecule has been effected. Bohr's

atom has been closely verified, both the first and second radiation potentials (10·1 and 12·2 volts, respectively), corresponding with the first two terms of the Lyman series having been obtained. Ionisation of the molecule is observed at 11·5 volts, and of the atom at 13·6 volts; dissociation of the molecule and radiation at 12·9 volts; and dissociation of the molecule with ionisation of one of its parts at 16·0 volts. The existence of two ionising potentials of the molecule has thus been conclusively proved, and the energy required for the dissociation of the molecule is shown to be equivalent to about 2·8 volts. A. A. E.

The Dielectric Constants of some Aqueous Solutions and their Explanation by the Dipole Theory of Debye. REINHOLD FÜRTH (*Ann. Physik*, 1923, **70**, 63—80).—The Drude method is employed, with aqueous alcohol and benzene as the calibrating liquids. The values for dextrose, lævulose, sucrose, carbamide, glycine, "saccharin," gelatin, albumin, and a number of substances of technical and biological importance are given. The Debye theory has been applied to correlate these results. If the dielectric constant of the solute is greater than that of the solvent, the increase in viscosity which occurs with increasing concentration should lead to three types of curves, and only one type would be anticipated if the dipole moment of the solute is smaller than that of the solvent. All three types of curves have been realised in this work. For colloidal solutions, the Debye viscosity formula is in good agreement with the results. For crystalline substances, it is not possible to derive the dielectric constant of the solute from the "mixture law." The dielectric constant of dilute solutions of electrolytes should be the same as for water, but should increase with increase in concentration. W. E. G.

The Conductivity of Highly Dissociated Binary Electrolytes. W. MUND (*Bull. Soc. chim. Belg.*, 1923, **32**, 156—178).—The Ghosh theory of electrolytes (T., 1918, **115**, 449, 627, 707; 1920, **117**, 823, 1390), although applicable to salts, does not appear to be sufficiently trustworthy in the case of acids and bases. The author's development of the theory leads to somewhat different results which are claimed to be more in accordance with the experimental facts; his final equation expresses as a function of the observed conductivity of an electrolyte, the ions of which have different mobilities, the work done in completely dissociating a gram-molecule of a symmetrical electrolyte at the same concentration. The general equation thus obtained closely resembles that of Ghosh (T., 1918, **115**, 455). An alternative equation is obtained by modifying the Ghosh equation by the factor 0·84. The latter is in close accord with many of the experimental cases studied, but scarcely applies to the case of acids and bases. The former gives results for these substances which agree with the experimental results. H. J. E.

Dissociation of Strong Electrolytes in Very Dilute Solutions. PHILIPP GROSS and OTTO REDLICH (*Z. physikal. Chem.*, 1923, **104**, 315—322).—A theoretical paper in which the validity of the law

of mass action in connexion with solutions of strong electrolytes is discussed along with the measurements of Washburn and his formulation of a dilution law (A., 1918, ii, 55, 56). The authors are of the opinion that whilst the measurements of the electrical conductivity of dilute solutions of potassium chloride by Washburn are not likely to be improved, yet they nevertheless do not give an unequivocal confirmation of his assumption $\lim_{c=0} dk/dc = 0$. On the other hand, these measurements do not disprove this assumption. It is thought to be unlikely that the validity or otherwise of Washburn's assumption can be furnished by direct experimental proof, but it may be furnished by the establishment of a theoretically deduced dilution law. J. F. S.

The Polarisation of Electrodes. II. J. E. VERSCHAFFELT (*Rec. trav. chim.*, 1923, 42, 332—336; cf. this vol., ii, 115).—A theoretical paper in which it is shown mathematically that there is, in electrolysis, no proportionality between the current density and the effective *E.M.F.* The author points out that, if his equation does not hold, the current density increases in smaller and smaller proportion to the increase of electromotive force, as if the resistance were increasing and finally tends towards a limiting value. In practice, this would only be observed in the case of electromotive forces much greater than those usually applied. H. J. E.

Ghosh's Theory of Strong Electrolytes. ADA PRINS (*Chem. Weekblad*, 1923, 20, 237—242).—A critical discussion of the theory, comparing actual experimental results with figures deduced from Ghosh's postulates. Agreement is good, but the theory needs extension and modification. S. I. L.

Electrometric Investigation of the Action of Normal Salts on the Potential of the Hydrogen Electrode. V. A. ARKADÉEV (*Z. physikal. Chem.*, 1923, **104**, 192—202).—The influence of normal salts on the potential of the hydrogen electrode has been investigated at ordinary temperatures (16—18°) by measuring the *E.M.F.* of the following elements: $H_2|0{\cdot}1N,HBr,KNO_3(c)||KCl||NKCl,Hg_2Cl_2|Hg$; $H_2|0{\cdot}1NHBr,KCl(c)||KCl||NKCl,Hg_2Cl_2|Hg$; $H_2|0{\cdot}1NHBr,KBr(c)||KCl||NKCl,Hg_2Cl_2|Hg$; $H_2|0{\cdot}1NHBr,NaCl(c)||KCl||NKCl,Hg_2Cl_2|Hg$; $H_2|0{\cdot}1NHBr,LiCl(c)||KCl||NKCl,Hg_2Cl_2|Hg$, and $H_2|0{\cdot}1NHBr,LiBr||KCl||NKCl,Hg_2Cl_2|Hg$. The influence of the normal salt is shown chiefly to consist in bringing about an increase in the potential of the hydrogen electrode which increases parallel with the concentration *c* of the normal salt. Only in the case of potassium nitrate and chloride is a slight change of potential observed in the opposite direction, and this is only when the concentration of the normal salt is small, (0·4—0·75*N*). For equivalent concentrations, the effect increases parallel with the ability of the normal salt to form hydrates (NaCl, LiCl, LiBr). Salts with the same anion as the acid of the electrode have a stronger influence than the corresponding salts of another anion, thus KBr and LiBr have a stronger effect than KCl and LiCl, respectively. The liquid contact potential in all the above measurements has been eliminated by

Bjerrum's method (A., 1905, ii, 793) which consists in using a bridge containing potassium chloride of concentrations 3·5*N*, 1·75*N*, and *N* and from the three values extrapolating the correction necessary to eliminate this value entirely. J. F. S.

The Slope of Current-Tension Curves in Electrolysis. A. H. W. ATEN (*Rec. trav. chim.*, 1923, **42**, 337—354).—A theoretical paper in which are represented curves showing the limiting current as a function of the concentration of an added indifferent electrolyte, the current density as a function of potential under different conditions, and ionic concentration as a function of current density. H. J. E.

Electrolysis of Bromine Solutions of Phosphorus Pentabromide. V. A. PLOTNIKOV (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 76—81; cf. A., 1915, ii, 508).—When electrolysed in bromine solution, phosphorus pentabromide gives rise to the ions P····· and Br′.

A 20% solution placed in an *E.M.F.* apparatus with platinum electrodes shows a steady current of about 97 milliamperes, the nature of the liquid remains unchanged, and there is no polarisation. When a current of 570 milliamperes is passed through the same solution, the temperature rises considerably, owing to the reaction between the liberated phosphorus kations and the solvent.

When a saturated solution is similarly electrolysed, the current, at first equal to 130 milliamperes, quickly drops down to 4 milliamperes; on reversing the current, it again becomes 130, but begins to drop in the same way; this is due to the formation round the cathode of a crust of phosphorus pentabromide which cannot dissolve in the already saturated solution.

The formation of Br′ anions is shown by means of Bruner and Bekier's silver electrodes (cf. A., 1912, ii, 732) when it is found that the cathode does not change in weight while the anode increases roughly in accordance with Faraday's law. G. A. R. K.

Electrolysis in Liquid Sulphur Dioxide. M. CENTNERSZWER and J. DRUCKER (*Z. Elektrochem.*, 1923, **29**, 210—214).—In continuation of the work of Walden and Centnerszwer (A., 1902, ii, 245), the authors have investigated the electrolysis of solutions of various iodides in liquid sulphur dioxide, employing a platinum gauze cathode. In the cases of a 5% solution of potassium iodide and a 2% solution of sodium iodide, electrolysed at about −20°, unstable products were formed at the cathode. Potassium or sodium, respectively, was probably first deposited, and combined with the solvent to form hyposulphite which then decomposed, forming thiosulphate and pyrosulphite. Whilst no deposition of sulphur at the cathode was observed in the case of these two solutions, such deposition did occur when pure dry liquid sulphur dioxide was electrolysed by means of a high tension current, confirming Walden's contention that positive sulphur-ions are formed by the electrolytic dissociation of liquid sulphur dioxide.

J. S. G. T.

Electrolytic Processes in the Presence of Colloids. I. The Electrolysis of Zinc Sulphate. NIKOLAI ALEXEIEVITSCH IZGARYSCHEV and P. S. TITOV (*J. Russ. Phys. Chem. Soc.*, 1917—1918, 49, 573—595).—The electrolysis of normal solutions of zinc sulphate was studied in the presence of varying amounts of gelatin or gum arabic, 1% of boric acid being added in all cases to prevent the formation of basic zinc sulphate; different current densities were used and the electrode (cathode) potentials were measured before and during the passage of the current, the results being expressed in the form of polarisation curves (cf. Izgaryschev, A., 1916, ii, 7); the viscosity and electrical conductivity of the solutions were noted at the same time. It is shown that a certain concentration of colloid corresponds with a maximum cathode polarisation and a minimum equilibrium potential; the same concentration corresponds with a break in the viscosity curves of the solutions, the viscosity increasing more rapidly with rise of concentration after that point. It is suggested that the colloid forms complexes with the kations of the electrolyte, a small amount of gelatin being associated with a large amount of zinc-ions, the proportions being about 1 : 100—200 by weight; the SO_4''-ions do not appear to form such adsorption compounds, probably because they are negatively charged like the particles of the colloid. The maximum polarisation corresponds with a point when all the zinc-ions present are adsorbed by the colloid to form the adsorption compound; further addition of gelatin to such a saturated solution produces little change. Similar results are obtained with gum arabic, with the exception that the viscosity curve shows no definite break. The effect of the colloid on the physical nature of the zinc deposited is discussed. G. A. R. K.

Electrolytic Processes in the Presence of Colloids. II. The Nature of the Metal-Colloid Complexes. N. A. IZGARYSCHEV (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 225—229).—The nature of the colloidal metal complexes formed during the electrolysis of zinc sulphate, in the presence of gelatin or of gum arabic, is discussed. It is shown that in the case of gelatin these complexes must be formed by adsorption of zinc-ions by the gelatin molecules, since in a normal solution of zinc sulphate containing 0·25 g. of gelatin per litre each molecule of the latter must have attached to it about 12,500 ions of zinc, whereas only 780 ions per molecule could be accounted for by chemical combination. In the case of gum arabic, however, in similar circumstances, only 21 zinc-ions are attached to each colloid molecule, this being probably less than the number of ions with which it could combine chemically, although, at the same time, adsorptive influences also play some part in the formation of the complex. R. T.

Electrolytic Processes in the Presence of Colloids. III. The Heats of Formation of Zinc-Gelatin Complexes. N. A. IZGARYSCHEV and P. C. TITOV (*J. Russ. Phys. Chem. Soc.*, 1918, 50, 230—236).—The heats of formation of zinc-gelatin complexes, formed during the electrolysis in an atmosphere of hydrogen of zinc

sulphate solutions containing gelatin, are measured. These heats are calculated from the Helmholtz equation connecting heats of formation with *E.M.F.* It is hence found that the heat of formation of such complexes is −2150 cal., this value being obtained with solutions containing equivalent quantities of the colloid, *i.e.*, with 0·025% solutions, whilst at greater concentrations greater heats of formation are found, due probably to heat of adsorption. The rate of adsorption of oxygen by solutions containing zinc dust is more than doubled by the addition of gelatin. R. T.

Electrolytic Processes in the Presence of Sugar. N. A. Izgaryschev and D. V. Stepanov (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 236—244).—The *E.M.F.* and anodal and cathodal polarisations obtained with zinc sulphate solutions containing various percentages of sugar are measured, and curves drawn showing the variations in these quantities as the proportion of sugar in the solutions varies. A maximum of polarisation is found, as when colloidal substances are used, but is much less distinct, and occurs with a 30% solution of sugar, whereas the same point is reached with a concentration of 2% of gum arabic or of 0·025% of gelatin. The curves for cathodal and anodal polarisation are symmetrical, and the values obtained are very close to each other. This is probably due to the action of the sugar being the same for both processes. From the curves, it is concluded that cathode process consists of the following: $(Zn, sugar)^{\cdot\cdot} \rightleftharpoons Zn^{\cdot\cdot} + sugar$, $Zn^{\cdot\cdot} \longrightarrow Zn$, whilst the anodal process is $(SO_4, sugar)'' \rightleftharpoons SO_4'' +$ sugar, $SO_4'' \longrightarrow SO_4$, $SO_4 + Zn \longrightarrow ZnSO_4$. The zinc sulphate forms a molecular compound with sugar in the ratio of 1 : 1. The conductivity of the solutions decreases rapidly with increasing concentration of sugar, and the presence of this substance does not affect the appearance of the metallic deposit obtained on the cathode. Similar measurements are made for zinc sulphate solutions containing brucine in place of sugar. This causes considerable polarisation, and the metal is deposited as a black sludge. R. T.

Electrolytic Processes in the Presence of Colloids. V. The Ultra-microscopical Examination of Metal-Colloid Complexes. N. A. Izgaryschev and (Mlle) K. S. Ponomareva (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 245—254).—Colloid-metal complexes, formed by the addition of gelatin or of gum arabic to zinc or copper sulphate solutions, are examined ultramicroscopically, and the number of particles and of aggregations of particles per square centimetre of the field of vision determined. The number of aggregations is found to increase with increasing concentration of the colloids, up to their characteristic concentration (0·025% for gelatin, and 2% for gum arabic), and then remains stationary, whilst the number of separate particles either remains the same, as in the case of gelatin, or decreases, as in the case of gum arabic. The gelatin particles are not visible under the ultramicroscope, but become plainly visible on the addition of the metallic salt, indicating that each particle must have increased in

magnitude as a result of adsorption of zinc- or copper-ions. Such particles exhibit cataphoresis on the passage of a current. R. T.

Action of Colloidal Gelatin on Electrolytic Cadmium. E. Milliau (*Bull. Soc. chim. Belg.*, 1923, **32**, 143—150).—Electrolysis of a solution containing cadmium as compared with a similar solution to which gelatin has been added shows that the addition renders the metallic deposit brighter and increases its hardness. H. J. E.

Low Voltage Arcs in Diatomic Gases. I. Hydrogen, Nitrogen, and Iodine. O. S. Duffendack (*Physical Rev.*, 1922, **20**, 665—687).—The current–voltage curves which have been obtained show that the breaking potential was always the ionising potential of the gas, namely, 16·3, 16·2, and 14·6 volts, respectively, the striking potential being greater. In the case of dissociated hydrogen and iodine, the arc could be maintained in normal and favourable circumstances, respectively, at 13·7, 10·0, and 12·1, 10·2 volts. The critical potentials agree with accepted results, and those associated with the atom and the molecule are experimentally distinguished. Spectroscopic investigations indicate that in the case of hydrogen the line spectrum is due to the atom and the band spectrum to the molecule. In the case of nitrogen, a flare was obtained which showed a strong spectrum of tungsten besides that of nitrogen (cf. Strutt, A., 1911, ii, 482); probably active nitrogen was formed. The positive bands appear to be due to the neutral molecule, the negative bands to the ionised molecule, and the lines to the atom. New negative bands were observed at 5075, 5018, and 4961 Å. In the case of iodine, the line spectrum only appeared in the arc. A. A. E.

The Evolution of the Molecule of Chromium Hydroxide in Contact with Water. (Mlle) Suzanne Veil (*Compt. rend.*, 1923, **176**, 1304—1305; cf. this vol., ii, 122).—The molecular coefficient of magnetisation of chromium hydroxide depends on the method of preparation. Variations in the value occur in the inverse sense to those obtained in the case of ferric hydroxide, but are smaller. H. J. E.

Photographic Registration of Critical Points and Irregularities in the Expansion of Liquids. C. Montemartini and L. Losana (*Gazzetta*, 1923, **53**, i, 89—94).—The authors describe an apparatus which, when adapted to the photographic registering device of Le Chatelier and Broniewski (*Rev. metall.*, 1912, **9**, 3, 134), permits of the accurate registration of singularities in the thermal expansion of liquids or solids and, hence, of rendering evident transformation points. A float suspended from one end of a balance beam is immersed in a liquid which can be gradually heated electrically. An adjustable counterpoise is attached to the other end of the beam, the oscillations of which are checked by means of a spiral spring. By means of a system of mirrors a ray of light is reflected from the beam on to a photographic plate, any irregularity in the expansion either of the material of the float or of the liquid being thus indicated. The apparatus has been applied

to the investigation of the maximum density of water, the expansion of sodium sulphate solution and of mixtures of quinine and cinchonine hydrogen sulphates, the allotropic transformation of sulphur, and the transformation of ammonium nitrate. T. H. P.

The Specific Heat of Carbon, Silicon, and Silicon Carbide at High Temperatures. A. MAGNUS (*Ann. Physik*, 1923, **70**, 303—331).—The copper block calorimeter has been employed for the determination of specific heats between room temperature and 900°. The specific heats of graphite, silicon, and silicon carbide, the heat of adsorption of graphite in air and water, and the coefficient of expansion of silicon carbide have been measured. The atomic heats of the diamond, silicon, and silicon carbide can be represented over a wide range of temperatures by means of a Debye function, in which only one value of the characteristic temperature Θ occurs, whereas for graphite an equation with two values of Θ must be employed. A comparison of the atomic heats of diamond and graphite shows that C_v for both modifications is identical at high temperatures. The measurements for silicon and carbon give a good example of the applicability of the Kopp-Neumann rule. The differences for SiC—(C+Si) are always positive between 350° and 1000°, reaching a maximum at 550°. At the ordinary temperature, the rule holds fairly well.

W. E. G.

Specific Heats of Polyatomic Gases at Low Temperatures. RUSSELL W. MILLAR (*J. Amer. Chem. Soc.*, 1923, **45**, 874—881).—The specific heats of methane, methyl chloride, boron trifluoride, and hydrogen sulphide have been determined from temperatures in the neighbourhood of the boiling point of the respective substances, to 5°. It is shown that the heat capacities of gases do not depend on the number of atoms in the molecule alone, but on the masses of the atoms, the constraints, and the temperature. In the case of hydrogen sulphide, the heat capacity increases with decreasing temperature, due to the heat of polymerisation and other causes. The following values of the ratio c_p/c_v and $c_{p'}/c_{v'}$ are recorded: methane, 278°, γ=1·32, γ_0=1·32, 199°, γ=1·35, γ_0=1·34, 158°, γ=1·41, γ_0=1·39, 142°, γ=1·42, γ_0=1·40; methyl chloride, 278°, γ=1·32, γ_0=1·30, 260°, 1·34, 1·31; hydrogen sulphide, 278°, γ=1·31, γ_0=1·30, 229°, 1·30, γ_0=1·28, 224°, γ=1·29, γ_0=1·27, 216°, γ=1·29, γ_0=1·26. The temperatures are absolute values. In the case of boron trifluoride, c_p=11·70 at 278° and 10·00 at 189°. J. F. S.

Chemical Constants of Saturation Equations. E. WERTHEIMER (*Z. physikal Chem.*, 1923, **104**, 203—232).—A theoretical paper in which the two chemical constants, a the entropy constant, and b, the energy constant, of thermodynamic functions have been investigated. The constant a is investigated by means of the vapour-pressure formula in which it appears in the form $a=Ri$, where R is the gas constant and i the Nernst chemical constant. When the vapour pressure is written in the usual form $\log_e p=f(T)$, it becomes necessary, on account of the different dimensions of

the variables, to specify exactly in what units (atm., mm. of mercury, etc.) the pressure is to be measured. The conventional chemical constant, i, is the numerical value with opposite sign, which the sum of the T containing quantities of the Nernst function assumes for any suitable pressure unit, $p=1$, $\log_e p=0$. For an ideal monatomic gas, the theoretical constant is the limiting value which the quantity i approaches asymptotically, when the pressure unit is chosen increasingly smaller, and in consequence the temperature integral of the specific heat of the solid substance vanishes. For the investigation of the energy constant, b, an isolated saturated vapour phase is considered by means of the equation $L\pm\varphi(b, v)$, in which a quantity of the same dimensions as energy also appears on the left-hand side; this is the energy of translatory motion of the molecules. In keeping with Bohr's hypothesis, the intramolecular energy of the molecule is introduced for b; $W=Nh\nu/2=-b$, and it is shown that in the case of a saturated vapour an equilibrium condition must exist between W and L. From this follow the well-known phenomena of spontaneous condensation and evaporation. The dependence of the value W on the temperature is briefly discussed. J. F. S.

Absolute Entropies and Chemical Constants. KARL F. HERZFELD (*Ann. Physik*, 1922, [iv], 69, 54—58).—A theoretical paper on the relationship between the methods of derivation of the entropy constants. The condition integral ϕ is recommended as the correct basis for the calculation of the entropies, which can then be obtained correctly from the classical theory for high temperatures, the introduction of the quantum theory being necessary for low temperatures. In order to obtain the same formula from the classical theory and the quantum theory, the phase volume must be measured, not in absolute units, but in cubes with content h'. In the methods due to Sackur, Tetrode, and Brody, the phase volume is measured more or less correctly, in unit cubes h^3, but in other methods, due to Stern and Tetrode, the phase volume is measured in cm.-g.-sec. and then divided by the phase volume of the "frozen" solid body, Nh^3. W. E. G.

The Equation of State for Methane Gas Phase. F. G. KEYES, L. B. SMITH, and D. B. JOUBERT (*J. Math. Phys. Mass. Inst. Tech.*, 1922, 1, 191—210).—A new apparatus is described for the measurement, by the isometric method, of the properties involving pressure, volume, and temperature of a gas the critical temperature of which is below 0°. The isometrics of methane are linear within the limits of experimental error between 0° and 200° up to 300 atm. Keyes's equation accurately represents the relations in question, as follows: $p=[4\cdot1175/(v-\delta)]T-[9802/(v+0\cdot565)^2]$, where T represents degrees Abs., and $\log\delta=0\cdot56195-(1\cdot05/v)$. The weight of 1 litre of methane calculated by the equation of state is 0·7718 at 0° and 760 mm. The coefficients of expansion at 1 atm. are calculated to be 0·0036796 at constant volume and 0·0036834 at constant pressure.

CHEMICAL ABSTRACTS.

The Thermodynamic Properties of Methane. F. G. KEYES, R. S. TAYLOR, and L. B. SMITH (*J. Math. Phys. Mass. Inst. Tech.*, 1922, **1**, 211—242).—From the experimental values of the vapour pressures and densities of liquid methane, determined over the entire liquid phase region by precision methods described in detail, a number of equations and thermodynamic constants are derived: (1) an equation for the vapour pressure as a function of the absolute temperature, $\log_{10}p(\text{atm.}) = -(595{\cdot}546/T) + 8{\cdot}09938 - (4{\cdot}04175\times 10^{-2}T)+(1{\cdot}68655\times 10^{-4}T^2)-2{\cdot}51715\times 10^{-7}T^3)$; (2) a mean density equation for calculating vapour densities near the critical point, $D_m=0{\cdot}16134+0{\cdot}00065723(T_c-T)$; (3) critical temperature 191·03° Abs., critical pressure 45·8 atm., critical volume 6·2 c.c./g.; (4) an equation for the heat of evaporation λ, from 100 to 150° Abs., $\log_{10}\lambda=1{\cdot}65214+2{\cdot}0076\times 10^{-4}(T_c-T)+0{\cdot}22225\log_{10}(T_c-T)$; (5) a linear relationship involving the internal energy change and the specific volume of liquid methane; (6) an equation for the specific heat of the vapour as a function of temperature and low pressure, $C_{p1}=0{\cdot}4288+1{\cdot}12\times 10^{-3}T-6{\cdot}45\times 10^{-6}T^2+13{\cdot}04\times 10^{-9}T^3+(93/T^2)p$; (7) the calculation from (6) and the usual thermodynamic equations of the specific heat of the liquid near the b. p. as 0·82 cal./g.

CHEMICAL ABSTRACTS.

A New Form of Melting-point Apparatus. H. A. BELL (*Ind. Eng. Chem.*, 1923, **15**, 375).—The apparatus is a modification of that of Thiele, and is made of pyrex glass. The thermometer, stirrer, and melting-point tube are inserted in a wide test-tube containing sulphuric acid, which itself rests in the heating apparatus. This consists of a bath of sulphuric acid with three vertical tubes. The middle and wider tube leads out of the bottom of the bath, and the two side tubes out of the top. The middle tube is heated by means of a coil of nichrome wire wound round it, the current being controlled by means of an electrolytic resistance. The heated acid ascends the middle tube and spreads out evenly over the walls of the test-tube containing the thermometer and the melting-point tube. The displaced liquid flows down the two outer tubes and a circulation is set up similar to that in Thiele's apparatus.

H. C. R.

Determination of Freezing Points of Substances. F. G. KEYES, B. TOWNSHEND, and L. H. YOUNG (*J. Math. Phys. Mass. Inst. Tech.*, 1922, **1**, 243—312).—The following freezing points are established: carbon tetrachloride, −22·87°; mercury, −38·90°; chlorobenzene, −45·58°; chloroform, −64·19°; ammonia, −77·80°; toluene, −95·70°; methyl chloride, −98·39°; methyl alcohol, −98·54°; carbon disulphide, −112·97°; ethyl ether (modification I), −123·40°; (modification II), −115·9°. Carbon dioxide has b. p. −78·53°, and oxygen has b. p. −182·94°.

CHEMICAL ABSTRACTS.

Vapour-pressure Measurements in Pure Argon. FRITZ BORN (*Ann. Physik*, 1922, [iv], **69**, 473—504).—The vapour pressure of solid and liquid argon have been measured from 65° K. to 90° K.

Considerable deviations between these values and those of Crommelin were found. The vapour-pressure curve agreed with the Nernst approximation formula. The heat of evaporation at the melting and boiling point and the conventional and true chemical constant were calculated from these results. The chemical constant for argon is $C=0{\cdot}79\pm0{\cdot}04$. W. E. G.

Reduction of the Vapour Pressure of some Metallic Salts in Aqueous Solution at 0°. C. Dieterici (*Ann. Physik*, 1923, [iv], **70**, 617—621).—The lowering of the vapour pressure of water by the solution of sulphates of lithium, manganese, cadmium, zinc, magnesium, and nickel, and the nitrates and chlorides of zinc, nickel, and cadmium, respectively, has been measured directly at 0° by enclosing the pure solvent on one side of an aneroid box and the solution on the other side. The measurements show that aqueous solutions of sulphates of low concentrations have a larger vapour pressure than corresponding concentrations of non-electrolytes such as carbamide and sucrose; at concentrations about $2N$ the two sets of solutions have about the same vapour pressure, and above this concentration the lowering of the vapour pressure by the sulphates is greater than in the case of the non-electrolytes. Solutions of nitrates give uniformly lower values for the vapour pressure than solutions of non-electrolytes. Chloride solutions behave in the same way as nitrate solutions, except that the deviation from the normal value is not so great. The present results are in keeping with the values found by Tammann for 100°.

J. F. S.

Calculations on Fractionating Columns from Theoretical Data. W. A. Peters, jun. (*Ind. Eng. Chem.*, 1923, **15**, 402—403).—An equation is derived giving the relationship between the composition of the vapour and of the liquid in equilibrium with it for binary mixtures of homologues, isomerides, and other similar liquids. With the aid of this equation, the distillation equation giving the compositions of a binary mixture of liquids before and after a certain portion has been distilled, in terms of the weights of material at the beginning and end of the distillation, can be integrated. An equation is also derived which gives the height of a fractionating column required to make any given separation of a binary mixture of liquids under given conditions of heat expenditure, composition of distillate, etc. H. C. R.

Relations concerning the Internal Heat of Vaporisation. J. E. Mills and P. K. Smith (*J. Physical Chem.*, 1923, **27**, 301—321).—In a previous paper (A., 1909, ii, 861) Mills discussed the internal heat of vaporisation in connexion with the equations (1) $\lambda=0{\cdot}000031833\,(dP/dT\,.\,T-P)(V-v)$ cal., (2) $\lambda=\mu'(\sqrt[3]{d}-\sqrt[3]{D})$ cal., and (3) $\lambda=CRT\log_e V/v=C\times4{\cdot}577/m\times T\log d/D$ cal. In these equations, $\lambda=L-29E=L-0{\cdot}00003183P(V-v)$ cal., L is the total heat of vaporisation of 1 g. of the liquid, λ the internal heat of vaporisation of 1 g. of the liquid, T the absolute temperature, P the vapour pressure in mm. of mercury V, the volume of 1 g. of saturated

vapour, v the volume of 1 g. of liquid, d the density of the liquid, D the density of the vapour, and μ' and C are specific constants. Equations 2 and 3 on combination give $\mu'(\sqrt[3]{d}-\sqrt[3]{D})=CRT\log_e d/D=CRT\log_e V/v$, and this has been transformed into $\mu'\sqrt[3]{d}+CRT\log_e v=\mu'\sqrt[3]{D}+CRT\log_e V$. The last equation has been examined by means of the existing data, which are tabulated, for diethyl ether, diisopropyl, diisobutyl, isopentane, n-pentane, n-hexane, n-heptane, n-octane, benzene, iodobenzene, carbon tetrachloride, and stannic chloride. The values for both sides of the equation have been calculated for a number of temperatures between 0° and the critical temperature and compared. It is shown that there is a remarkably exact agreement between the two quantities when the factor $\mu'\sqrt[3]{D}$ is greater than $3/2RT$. J. F. S.

Some Properties of Ideal Gases. PAVEL N. PAVLOV (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 322—327; this vol., ii, 380). —It is proved that for ideal gases, in corresponding conditions, the pressure is proportional to the absolute temperature. A formula shown previously to hold for normal liquids is applicable also to ideal gases, the critical temperature of which is given by the expression $T_c=1\cdot6167M\sqrt{n}$, where M is the molecular weight of the gas and n the number of atoms in its molecule; whilst the critical pressure, p_c, is $0\cdot13076M\sqrt{n}$. The expression $(p/T)_{corr.}$ is found to be equal to 0·003663 for all gases examined. From this, and since $pv=RT$, it follows that the corresponding volumes of gases must be equal, *i.e.*, that a mole of any ideal gas must occupy the same volume, at 0° and 760 mm., as well as at corresponding temperatures and pressures. Nitrogen, oxygen, nitric oxide, and hydrogen give values in close agreement with this rule, whilst carbon dioxide and hydrogen chloride give deviations of up to 1·6%. R. T.

The Molecular Condition of Pure Liquids. NIKOLAI ALEXANDROVITSCH KOLOSOVSKI (*J. Russ. Phys. Chem. Soc.*, 1917—1918, **49**, 613—616; cf. Pavlov, A., 1917, ii, 125, 293, 358).—Pavlov's conclusion that in corresponding states all normal liquids have the same molecular volume is shown to be due to mathematical error. His criticism of Kistiakovski's rule (A., 1906, ii, 655; 1913, ii, 831), which has a theoretical basis, is also shown to be unfounded. G. A. R. K.

The Molecular Condition of Pure Liquids. PAVEL NIKOLAEVITSCH PAVLOV (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 463—464).—It is shown that Kolosovski's objections to the formulation of the molar suface of a liquid as v^n, where $v=m/d$, and m is the molecular weight of the liquid, d its density, and n is a constant, are devoid of foundation. R. T.

Einstein's Formula ($\eta/\eta_0=1+2\cdot5\varphi$) and the Viscosity of Tannin Solutions. A. V. DUMANSKI and B. K. TARASOV (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 186—192).—A formula deduced by Einstein, $\eta/\eta_0=1+2\cdot5\varphi$, where η is the internal friction of the solution, η_0 that of the solvent, and φ is the volume occupied by the

solute per c.c. of the solution (*Ann. Phys.*, 1911, [iv], **34**, 391), is tested for the case of sols, tannin sol being selected for this purpose. A new symbol, φ_1, the volume of 1 g. of solute, is introduced, φ being equal to $\varphi_1 c$. The relative viscosities, η/η_0, of tannin solutions are measured at 20°, 40°, 60°, and 80°, and φ, hence, and also from the density of tannin alone, calculated for various concentrations, ranging from 0·0025 g. to 0·25 g. of solute per c.c. of solution. φ_1 is found not to be constant, but to increase with the concentration of tannin, and is greater, in general, than the corresponding value calculated from the density alone. At higher temperatures, the values of φ_1 obtained are much closer to one another than at lower temperatures. The varying values obtained are due, partly to the formulæ used in their calculation being only approximate, and partly to adsorption of solvent on the particles, causing an increase in their size. A further cause is probably the retardation of the free movement of the particles by the solution, so that when they move they carry a portion of the solution with them, producing a so-called hydrodynamic volume of the particles. This envelope of solvent becomes smaller at higher temperatures, and the values of φ_1 become correspondingly smaller. A modified form of the Einstein formula, $\eta/\eta_0(1 + Kc^2) = 1 + 2{\cdot}5\ \varphi_1 c$, is proposed, where K and c are constants, and in this form the equation agrees well with experimental results. R. T.

Stalagmometry and Viscosimetry. F. V. VON HAHN (*Chem. Ztg.*, 1923, **47**, 402).—A description is given of a new type of viscosistalagmometer. The instrument, by means of which two immediately consecutive measurements can be made of the rate of flow through the capillary, and of the number of drops from the end of the capillary, consists of a modification of Ostwald's viscosimeter in which the capillary tube with a carefully ground dropping surface fits into the U-shaped reservoir by means of a ground glass joint, and a second tube filled with a glass cock at its upper end is fused into the reservoir close to the lower exit of the capillary. In use, the liquid is forced up into the bulb in the upper part of the capillary, the cock in the second tube being closed, and the rate of flow through the capillary is then measured. On opening the cock, the level of the liquid falls below the capillary exit, and the contents of bulb and capillary then drop from the prepared surface of the latter, and the number of drops can be ascertained without having to remove the liquid from the apparatus or subject it to any change of temperature. An example of the use of the apparatus is given in a determination of the viscosity and stalagmometric curves of a paraldehyde–water mixture at different temperatures, and of an albumin–water mixture. G. F. M.

Adsorption from the Gas Phase at a Liquid-Gas Interface. THOMAS IREDALE (*Phil. Mag.*, 1923, [vi], **45**, 1088—1100).—A critical *résumé* of the drop-weight method of determining surface tension is given, and from the results of Harkins and Brown (cf. A., 1919, ii, 221) the ratio of the radius of the drop to the radius of the tube from which it falls have been calculated, and a method is

given for ascertaining, from these ratios, the surface tension of any liquid. The surface tension of mercury in contact with methyl acetate vapour at varying partial pressures has been measured by the drop-weight method. The surface tension is depressed rapidly at first and then more slowly as the partial pressure is increased, until at 62 mm. it becomes practically constant. Beyond 227 mm., the value of the surface tension suddenly falls off to that of the interfacial tension of mercury in contact with liquid methyl acetate. The horizontal portion of the curve corresponds with complete saturation of the surface with an adsorbed film. This film contains $4\cdot5 \times 10^{-8}$ g. of methyl acetate per sq. cm., and each molecule occupies 27×10^{-16} sq. cm., which is nearly the space occupied by a molecule of fatty acid on the surface of water.

W. E. G.

The Molecular State of Pure Liquids. IV.—VII. PAVEL NIKOLAEVICH PAVLOV (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 304—322; cf. A., 1917, ii, 125, 293, 358).—For normal liquids the surface tension, at corresponding absolute temperatures, *i.e.*, at temperatures which give equal values on division by the corresponding critical temperature, is deduced to be a function of the product of the molecular weight into the square root of the number of atoms in the molecule. This is formulated as follows: $M\sqrt{n}/\gamma_{\text{corr.}}=$ a universal constant. This law is shown to hold for ethyl ether and carbon tetrachloride, over a range of temperatures in which no dissociation or association is known to take place. Propyl formate gives values very close to those calculated on the above law, showing that it deviates little from the normal, whilst water, *n*-octane, benzene, methyl formate, methyl alcohol, and acetic acid vary more widely. For associated liquids, the function $M\sqrt{n}/\gamma_{\text{corr.}}$ is smaller than for normal liquids, whilst with dissociated liquids it is greater. This function gives, therefore, an indication of the degree of association or dissociation of liquids. A formula for the calculation of the density of liquids or their saturated vapours is deduced, as follows: $d_{\text{corr.}}\sqrt{n}/T_{\text{corr.}}=$ a universal constant, where $T_{\text{corr.}}$ is the corresponding absolute temperature, $d_{\text{corr.}}$ the density at this temperature, and n is the number of atoms in the molecule. This law holds for ethyl ether and carbon tetrachloride, and deviates little in the cases of ethyl acetate, propyl formate, and methyl propionate, whilst for water and *n*-octane greater deviations exist. The expression $M\sqrt{n}/T_{\text{corr.}}$ is shown to be equal to a constant for normal liquids, and hence it follows that $T_{\text{corr.}}$ must increase with association and decrease with dissociation. At the critical absolute temperature, the above expression is for normal liquids equal to 0·6185, and the critical temperature of such liquids is therefore given by the expression $T_c=M\sqrt{n}/0\cdot6185$. The critical temperatures of carbon tetrachloride, ethyl ether, and some esters agree well with those calculated from this formula, whilst the critical temperature of water, actually 647° Abs., is calculated to be 50·4° Abs., showing that a high degree of association exists. Normal liquids are

shown to have, at corresponding temperatures, the same molar volume. R. T.

Adsorption at Liquid-Vapour, and Liquid-Liquid Interfaces and some Related Phenomena. H. H. KING (*Kansas Agr. Exp. Sta. Tech. Bull.*, 1922, **9**, 1—39; cf. King and Wampler, A., 1922, ii, 741).—The adsorption was calculated by plotting the surface tension at various concentrations against the logarithm of the concentration and applying Gibbs's equation. In the determination of surface tension by the drop-weight method, the weight of a hanging drop was found to depend on its time of formation, the explanation being found in the application of Fick's law. The adsorption in the liquid-vapour interface in mols. per sq. cm., the number of mols., the area occupied by each, and their diameters are given for the first ten acids of the aliphatic series, and certain alcohols, amines, and esters. The alcohols exhibit a greater adsorption than the acids, possessing also a constant degree of adsorption through a greater range of change of concentration, a difference which may be explained by the difference in electrolytic character. C_4 and C_5 alcohols and acids reach zero adsorption at the same respective concentration, whilst C_1, C_2, and C_3 alcohols show adsorption at lower concentrations than do the corresponding acids. The curves for the esters lie in nearly the same position as those of the alcohols with the same number of carbon atoms, and on the whole they correspond closely with those of the acids. Ethyl propionate requires a higher concentration than propyl acetate to produce the same adsorption. The more symmetrical is the ester, the smaller is the adsorption after it has once become constant. Experiments with butyric acid solutions show that the fugacity of the molecules in the interface water-benzene is three times as high as that on the surface of water when both films have the same concentration of about 10^{14} mols. per sq. cm. The adsorption of substances of the type of organic acids, alcohols, and esters is always greater at the surface of water than at the interface between water and an organic solvent of the type of benzene or a paraffin hydrocarbon. Single molecules of butyric acid appear to be more soluble in water than in benzene, whilst for double molecules the reverse is the case. The presence of benzene as an upper layer does not change the number of butyric acid molecules in this unimolecular layer. CHEMICAL ABSTRACTS.

Adsorption of Carbon Monoxide and Hydrogen by Platinised Asbestos. FRANK HOWELL POLLARD (*J. Physical Chem.*, 1923, **27**, 356—375).—The adsorption of hydrogen, carbon monoxide, and mixtures of the two gases by platinised asbestos has been determined at 0° for pressures up to 1 atm. The determination of the actual adsorption isotherms is made difficult by the fact that minute quantities of impurities, such as may be entrained by passing the gases through stopcocks lubricated by grease, decrease greatly the adsorptive power of the platinum. The observations of Berliner in this respect have been fully confirmed (*Ann. Phys. Chem.*, 1888, [ii], **35**, 791). It appears probable that

all determinations of the adsorption of gases by platinum are untrustworthy unless scrupulous care be taken to eliminate all possible contamination of the adsorbent. The adsorption process is a reversible one, provided that sufficient time is allowed to elapse for the establishment of equilibrium. The adsorbed gas may be removed completely from the platinum by long-continued pumping at 0°. No evidence has been obtained supporting the contention that the gases under investigation form definite solid compounds with platinum at this temperature. When contamination of the adsorbent is most effectively prevented, platinised asbestos is able to adsorb two hundred volumes of hydrogen or three hundred volumes of carbon monoxide at 0° and atmospheric pressure, the volumes of gas being expressed in terms of the volume of platinum present. Carbon monoxide, added in relatively small amounts to the system hydrogen-platinised asbestos in equilibrium, is able to displace completely the adsorbed hydrogen from the platinum. This fact supports directly Bancroft's hypothesis of catalytic poisoning (A., 1917, ii, 566), and accounts for the fact that carbon monoxide is known to be a poison toward platinum in certain catalytic hydrogenations. The adsorption coefficient of two hundred volumes of hydrogen is greater than that obtained by previous investigators, who used platinum black instead of platinised asbestos. The greater value now obtained is doubtless the result, at least partly, of the greater precautions taken to prevent contamination of the catalyst, but it may indicate also that platinum in the form of platinised asbestos has a greater specific surface than platinum as platinum black. J. F. S.

Adsorption of Gases by Oxide Catalysts. Arthur F. Benton (*J. Amer. Chem. Soc.*, 1923, **45**, 887—899).—The adsorption of carbon dioxide, oxygen, hydrogen, and carbon monoxide by copper oxide, manganese dioxide, cobalt sesquioxide, ferric oxide, vanadium pentoxide, silica, and Hopcalite (60% manganese dioxide and 40% cupric oxide) has been measured at 1 atm. pressure and at temperatures from −79° to 184°. The catalysts were prepared under conditions which were as nearly as possible analogous in the different cases. A method was devised whereby a correction could be obtained for the absorption which occurs in some cases and for the progressive chemical reaction which occurs with hydrogen and carbon monoxide, and in this way the true adsorptions were obtained. Two different types of adsorption, termed "primary" and "secondary" adsorptions, are discussed in connexion with these and other measurements. Secondary adsorption is the type which occurs with inert adsorbents, and depends on secondary valency. The melting points of the adsorbent and the adsorbed substances are a measure of the forces involved. Primary adsorption, on the other hand, occurs with active adsorbents, and depends on primary valency forces. In common with other manifestations of chemical affinity, primary adsorption is specific. The form of the adsorption isotherms and isobars is very different for the two types. In certain of the present measurements, both kinds of

adsorption occur simultaneously. A method is devised for distinguishing between the two types and estimating the extent of each, in such cases. The experiments allow the following general statements to be made; the secondary adsorption of different gases is in the order of their melting points; the secondary adsorption by different adsorbents is also in the order of their melting points, and the primary adsorption of carbon monoxide is approximately in the order of the relative reducibility of the different oxides.

J. F. S.

Adsorption and Catalysis in Carbon Monoxide Oxidation. ARTHUR F. BENTON (*J. Amer. Chem. Soc.*, 1923, 45, 900—907; cf. preceding abstract).—The connexion between adsorption and catalytic activity of a number of oxides for carbon monoxide has been investigated in view of the results previously published (*loc. cit.*). It is shown that neither the secondary adsorptions nor the total adsorptions by different oxide catalysts bear any relation to their relative catalytic activities. The primary adsorption of carbon monoxide is, however, in exactly the same order as the catalytic activity. The mechanism of reduction of an oxide by a reducing gas is discussed as a three-stage process involving adsorption, isomeric change, and evaporation of the product from the surface of the oxide. Several possible methods are discussed in which the catalytic oxidation of carbon monoxide in contact with active metallic oxides might occur, and it is shown that only the mechanism based on alternate reduction and reoxidation is in satisfactory agreement with adsorption data. Bone and Wheeler's experiments on the catalytic combination of hydrogen and oxygen in the presence of metallic oxides, from which they drew the conclusion that this process does not depend on alternate reduction and reoxidation (A., 1906, ii, 434), are considered in connexion with the present results and are shown to support the present view rather than to discredit it. J. F. S.

Some Factors Governing the Complete Sorption of Iodine by Carbon from Chloroform Solution. JAMES BRIERLEY FIRTH and FRED SHEASBY WATSON (T., 1923, 123, 1219—1222).

Adsorption. XIII. Hysteresis of the Degree of Hydration of Vegetable and Animal Charcoals. ADAM VLADISLAVOVITSCH RAKOVSKI (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 371—380).—Various kinds of vegetable and animal charcoals are dried to constant weight by keeping in a desiccator over concentrated sulphuric acid. The charcoal is then allowed to absorb water vapour, and curves are drawn of which the abscissæ are pressure of water vapour and percentage weight of water adsorbed. If such hydrated charcoals are dried in an analogous way, by gradually reducing the pressure, the whole of the water cannot be removed, 2% remaining in the charcoal after drying to constant weight. The dehydration curve exhibits, therefore, a certain constant lag behind the hydration curve. If now sugar charcoal thus treated is again allowed to adsorb water, and again dried, no further hysteresis is noticeable,

the last three curves being almost identical. In the case of animal charcoal, the second hydration curve occupies a position intermediate between the first hydration and dehydration curves. The water thus retained by the charcoal is only to a small extent given up by heating at 110°. Since the original samples used are only comparatively dry, such hydrated charcoal may contain up to 17% of water, which is not entirely expelled even by heating to redness in a current of nitrogen, and probably is chemically combined with the carbon. Charcoals are not, therefore, appropriate substances for the study of the phenomena of adsorption, as their exact action varies with the nature of the charcoal used, and with its past history. R. T.

Anomalous Osmosis of Solutions of Electrolytes with Colloidal Membranes. II. Effect of Stirring the Solutions. F. E. BARTELL and D. C. CARPENTER (*J. Physical Chem.*, 1923, **27**, 346—355; cf. this vol., ii, 221).—The effect of stirring or rocking on the osmosis of solutions of potassium ferricyanide, sulphate, and chloride, aluminium and calcium chlorides with collodion membranes has been investigated and the osmosis-concentration curves have been compared with those obtained when the solution is not stirred. It is shown that the shape of the initial osmosis-concentration curves and the maximum osmosis-concentration curves was of the N-type throughout for potassium salts and was more strongly accentuated than when the solutions were not stirred. With dilute solutions, stirring increased both the initial and the maximum osmotic effects in the case of potassium chloride, calcium chloride, and potassium sulphate, but decreased the effect with aluminium chloride and the maximum effect with potassium ferricyanide. With concentrations of electrolytes greater than $0{\cdot}1M$, stirring has but little influence on either the initial or maximum osmosis. Stirring produced a tendency towards the N-shaped curve even in the case of aluminium chloride, a tendency which had not hitherto been observed. With sucrose solutions, stirring increased the rate of the initial osmosis, but decreased the maximum osmosis. The whole of the above results are in keeping with the view that the passage of the solute through the membrane is largely responsible for the appearance of the N-shaped curve in osmosis through collodion membranes. Stirring increases the rate of passage of all electrolytes through a collodion membrane at all concentrations. The rate of passage of solutes into water is greater for concentrated solutions than for dilute solutions, but it is not proportional to the concentration except in two cases with calcium chloride. In the region of $0{\cdot}01\ M$, the percentage increase in g.-mols. of salt passing through the membrane in two hours, due to stirring, is as follows: potassium chloride, 140; potassium sulphate, 13; potassium ferricyanide, 63; calcium chloride, 72; aluminium chloride, 95. The ratio of the concentrations of solute in the two compartments decreased in magnitude as the osmosis progressed. In concentrated solutions, this ratio approached 1:1 at the maximum osmosis period, but for more dilute solutions the

ratio remained much greater. With potassium salts, the relation of anion valency to the rate of passage of electrolyte through the membrane showed the following order in each case:

$$Cl' > SO_4'' > Fe(CN)_6'''.$$

This order was the same at all concentrations, and was the inverse of the order of magnitude of maximum osmosis. With chlorides, the kation order was $K^{\cdot} > Ca^{\cdot\cdot} > Al^{\cdot\cdot\cdot}$ at all concentrations. The above series are the same as those obtained when the solutions are not stirred. J. F. S.

Diffusion of Dyes into Gels. I. TRAUBE and M. SHIKATA (*Kolloid Z.*, 1923, **32**, 313—316).—The distance which 0·1% solutions of azo-blue, Congo-red, water-blue, naphthol-green, Bordeaux-R, acid-violet, acid-green, eosin, azorubin, naphthol-yellow, tannin-heliotrope, night-blue, methylene-blue, and rhodamine diffuse into gelatin gels (2·5, 5, 7·5, 10·0, 12·5, 15·0, 17·5, and 20%), agar-agar gels (0·5, 0·75, 1·0, 1·25, 1·5, 1·75, and 2·0%), and soap gels (2·5, 5, 7·5, and 10%) in forty-eight hours has been measured. The results show that $C^{1/3}D=K$, where $C^{1/3}$ is the mean distance between two gelatin particles, D the distance travelled by the diffusing solution, and K is a constant. Put into words, this means that the mean distance travelled by a dye particle, in a given time, in gelatin gels of various concentrations is proportional to the mean distance between the gelatin particles. This rule does not hold for agar-agar or soap gels. J. F. S.

Velocity of Diffusion in Jellies during a Simultaneous Chemical Change. MANJIRO WATANABE (*Kolloid Z.*, 1923, **32**, 320—328).—During experiments on the formation of precipitates in jellies, the distance, x, which a substance, diffusing from a limited quantity of a solution, travels in a time z into a jelly was measured, when at the same time a limited amount of chemical change is taking place with another substance dispersed throughout the jelly. In the case of diffusion from an unlimited amount of solution when no chemical change is taking place, the velocity coefficient $x/z^{1/2}$ is constant for a given preparation; in the present case, this factor is not constant, but changes with the time. On plotting the value, it is shown to change according to a regular curve, which in most cases is almost a straight line. As a first approximation, this line may be represented by $x/z^{1/2}=(Z-z)Z\,.\,k$, where k is the velocity coefficient for the commencement of the process and Z a constant for a given preparation. If the formula were strictly true, Z would be the time which had elapsed from the commencement of the process to the "critical time" where the direction of the precipitate formation reverses. The equation has been examined for various concentrations of the jellies (gelatin) which contained various quantities of lead nitrate and sodium sulphide, the diffusing solutions being ammonia, ferrous sulphate, and copper sulphate. J. F. S.

An Apparent Deviation from Henry's Law for the System, Ammonia-Water. G. CALINGAERT and F. E. HUGGINS, jun. (*J. Amer. Chem. Soc.*, 1923, **45**, 915—920).—The ratio of the

composition of vapour and liquid phase has been determined for ammonia-water solutions at the boiling point for concentrations from 0·005 g. to 1·250 g. of ammonia per litre. A deviation from Henry's law has been observed which might be attributed to the electrolytic dissociation of the ammonia. It has been shown that a solution of maximum boiling point must exist for the system ammonia-water, the composition of which is 0·000010 g. of ammonia per litre, and that the distillation curve of this system must be similar to that of hydrochloric acid and hydrobromic acid solutions, the only difference being that, on account of the high degree of dissociation of the acids, the maximum boiling point of their solutions corresponds with a much higher concentration than in the system ammonia-water where the degree of dissociation is very small.

J. F. S.

Piezo-chemical Studies. XVIII. A General Direct Process for the Determination of Solubility at High Pressures. ERNST COHEN, D. H. PEEREBOOM VOLLER, and A. L. TH. MOESVELD (*Z. physikal. Chem.*, 1923, **104**, 323—331).—A process is described whereby the solubility of solids may be determined at high pressures with the same accuracy as is possible at ordinary pressure. The method consists in placing a supersaturated solution of the salt under investigation in one half of a double pipette, the other half being filled with benzene; this is placed in one limb of a steel U-tube and the pressure generated in the steel tube as previously described (A., 1919, ii, 321). The U-tube is then fixed on an axis horizontally in an oil thermostat and given a rocking motion whereby a small quantity of mercury rolls backward and forward, producing an efficient mixing of the solution. After shaking for about twenty hours, the rocking is stopped and the U-tube brought into the vertical position, so that the undissolved solid falls to the bottom of the lower pipette; the solution is then forced under pressure into the upper pipette, which until now had been filled with benzene. The pressure is then rapidly reduced to atmospheric and the pipette removed. Its contents are weighed and analysed as in ordinary determinations. Full manipulative directions are given in the paper. The method has been applied to the determination of the solubility of thallous sulphate in water at 30° and at pressures of 500, 1000, and 1500 atm. The following results are recorded in grams per 100 g. of saturated solution: 1 atm., 5·83; 500 atm., 7·48; 1000 atm., 9·03, and 1500 atm., 10·50, each value being the mean of two very close determinations. The influence of pressure on the solubility of thallous sulphate is given by either of the equations $C=5{\cdot}831+0{\cdot}003377p-0{\cdot}000000175p^2$ and $C=5{\cdot}831+0{\cdot}003295p-0{\cdot}000000109p^2$. The present experiments show that increase in pressure has a considerable influence on solubility (cf. Cohen, *loc. cit.*).

J. F. S.

The Distribution of Solvent between Solutes. VI. The Optical Rotation of Solutions of Sugar with Salts. ANTON GRIGOREVITSCH DOROSCHEVSKI (*J. Russ. Phys. Chem. Soc.*, 1917, 49, 408—413; cf. A., 1913, ii, 1014; 1914, ii, 419, 610; 1916, ii, 121).—The

relative densities and optical rotations of solutions containing sugar and various salts of alkali and alkaline-earth metals are calculated from a formula put forward by the author in his preceding articles, and found to agree well with experimental results for dilute solutions. It is shown that the theory previously mentioned, as to the distribution of a solvent between substances dissolved in it, explains why the addition of such salts to sugar solutions increases the angle of optical rotation to an extent which increases with increasing molecular weight of the salt. R. T.

The Distribution of Solvents between Solutes. V. The Specific Gravities and Refractive Indices of Mixed Solutions. A. G. DOROSHEVSKI and E. N. EKAREVA (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 64—76; cf. A., 1915, ii, 408; 1916, ii, 121).—The deviations of the conductivities from the calculated additive values which are observed on mixing aqueous solutions of two electrolytes have been accounted for on the assumption that the solvent is divided between these electrolytes in proportion to their chemical masses.

It is now shown that specific gravities and refractive indices of mixed solutions obey the same law, and that these properties can be readily calculated for a given solution, provided, of course, there is no chemical interaction between the dissolved substances. The formula used for calculating the density d_0 of the mixed solution is $d_0 = \{100(am'd + a'md') - aa'(d-d')(m'-m)\}/(am' + a'm)$, where a and a' are the weights of the two solutes in 100 g. of mixed solution, m and m' their gram-equivalents, and d and d' the "partial" densities of their respective solutions. The same formula, substituting n_0, n, and n' for d_0, d, and d', applies to refractive indices. The calculated values are shown to be in good agreement with experimental data for a number of mixed solutions such as potassium and sodium chlorides, methyl and ethyl alcohols, etc. G. A. R. K.

Eutectic Points in Salt Solutions. PAUL MONDAIN MONVAL (*Compt. rend.*, 1923, **176**, 1313—1316).—An attempt to verify experimentally the generalisation of Le Chatelier, that at the eutectic point the trigonometrical tangents to the two curves are in the ratio of the latent heats of solutions of weights of the two substances equal to those present in the saturated solution, showed that its validity is approximate. Certain discrepancies observed probably correspond with experimental errors. The author has used for this work the heats of solution previously determined by him (this vol., ii, 295) and his observations extend to the nitrate, chloride, and sulphate of potassium, nitrate of sodium, and the nitrate and chloride of ammonium. H. J. E.

The Factors Influencing Compound Formation and Solubility in Fused Salt Mixtures. JAMES KENDALL, E. D. CRITTENDEN, and H. K. MILLER (*J. Amer. Chem. Soc.*, 1923, **45**, 963—996; cf. Kendall and Booge, A., 1918, ii, 37; Kendall and Gross, A., 1922, ii, 33, and Kendall, Davidson, and Adler, A., 1922, ii, 34). —The freezing-point curves of fifty binary fused salt mixtures

have been investigated and the existence of forty-nine new additive compounds has been established. The binary mixtures examined were, aluminium bromide with the bromides of lithium, sodium, potassium, ammonium, silver, calcium, barium, magnesium, zinc, cadmium, mercury, thallium, carbon, tin, lead, phosphorus, arsenic, antimony, bismuth, chromium, manganese, nickel, and iron, respectively; aluminium chloride with the chlorides of lithium, sodium, potassium, ammonium, copper, silver, barium, magnesium, mercury, thallium, tin, antimony, chromium, and manganese, respectively; and antimony trichloride with the chlorides of lithium, sodium, potassium, ammonium, copper, silver, barium, tin, and mercury, respectively. The factors effecting compound formation in the above systems have been critically examined. As in the previous work (*loc. cit.*), the diversity of the constituent radicles of the components has been found to be the main influence. Other factors discussed are valency, unsaturation, position in the electrode potential series, temperature, internal pressure, atomic volume, atomic number, and association. Very unusual curves are encountered in the systems sodium bromide–aluminium bromide and stannic chloride–antimony trichloride. In the former of these, a compound breaks up into two partly miscible layers when heated, and its true melting point cannot be ascertained. In the latter, an exceedingly small change in the temperature of fusion over a wide composition range is induced by the existence of a two-liquid layer region just below the freezing-point curve. J. F. S.

Molecular and Crystal Symmetry. T. V. BARKER (*Nature*, 1923, **111**, 632—633; cf. Shearer, this vol., ii, 223; Fedorov, A., 1913, ii, 305).—A discussion of the Fedorov–Shearer principle of the conservation of symmetry. It is pointed out that for the expression $n/m=p$, where n is the "symmetry number" of the structural unit (the number of identical or enantiomorphously related asymmetric parts into which it is subdivisible), m the number of molecules it contains, and p the symmetry number of each molecule, arbitrary and unanticipated values of p must be chosen in order to apply the principle. The case of tartaric acid is discussed in detail, and it is suggested that the structure is not simply built up of a single space-lattice arrangement, with the molecular axes uniting to create the symmetry axis of the crystal, but is formed of a pair of molecular lattices, mutually interpenetrating. The second is held to restore the symmetry lost by a refusal of the crystal to recognise molecular symmetry; if this is so, the Fedorov–Shearer principle is infringed. It is admitted, however, that the crystals of tartaric acid are too complicated to be of effective use in testing the principle; carbon tetrabromide, carbon tetraiodide, hexachloro- and hexabromo-ethane and stannic iodide would be preferable. A. A. E.

Dielectric Constants of Colloidal Solutions. III. J. ERRERA (*Kolloid Z.*, 1923, **32**, 240—246).—A continuation of previously

published work (A., 1922, ii, 694; this vol., ii, 225). The time required for the coagulation of alcosols of mercuric sulphide, cupric sulphide, and platinum by the addition of liquids of varying dielectric constant has been determined, with the liquids benzene (2·26), carbon tetrachloride (2·25), toluene (2·51), *iso*amyl alcohol (5·7), *iso*butyl alcohol, (18·6), ethyl alcohol (25), methyl alcohol (33), nitrobenzene (35·5), water (81), chlorobenzene (5·5), xylene (2·32), hexane (1·85), acetone (21), chloroform (4·95), and ethyl ether (4·36). The figures in brackets are the dielectric constants of the liquids. Further experiments with mixtures of the liquids named with varying quantities of ethyl alcohol were also carried out. The experiments show that the addition of liquids of dielectric constant greater than that of the dispersion medium has no coagulating influence on the sol. Liquids with a dielectric constant smaller than that of the dispersion medium coagulate the sols, and in most cases the smaller the dielectric constant the greater is the coagulating power of the added liquid. Cupric sulphide alcosol, both alone and when mixed with ten times its volume of benzene, is shown by migration experiments to be negatively charged. Cupric sulphide alcosol on coagulation changes its colour from dark brown to an intense olive-green. The dielectric constant of colloidal solutions, where solvation has taken place to only a slight extent, is the same as that of the dispersion medium. Vanadium pentoxide sol is, however, exceptional; here the dielectric constant is 1280 as against 81, the value of the dispersion medium water. The effect in this case is probably connected with the well-known optical anisotropy. In certain cases, the dielectric constant has an effect on the preparation and swelling of colloidal systems. J. F. S.

Attempt to Formulate a Theory of the Kinetics of the Process of the Solution of Colloids. N. P. PESKOV (*Kolloid Z.*, 1923, **32**, 232—238).—An attempt is made to formulate a mathematical hypothesis of the kinetics of the solution of colloids. Two formulæ have been developed from theoretical considerations, and these have been tested in connexion with a series of gold sols. These expressions have the form $K=1/t\,.\,\delta/\pi r_0C^{2/3}\,.\,\{1-(1-\alpha)^{1/3}\}/(1-\alpha)^{1/3}$, and $K=1/4\,.\,\delta/\pi r_0C^{2/3}[q\,.\,2{\cdot}3\log\{1+q(1-\alpha)^{1/3}/(1+q)(1-\alpha)^{1/3}\}]$, where K is the velocity constant of the solution process, r_0 the radius of the colloidal particles at the commencement of the process, δ the density of the colloid, C the colloid concentration, that is, the number of colloidal particles in the unit volume, t the time, α the degree of solution at the time t, and $rq=r_0$, where r is the radius of the molecule. Preliminary experiments showed that the kinetics of the solution of colloids is very different from that of macro-heterogeneous solutions, and also from that of molecular disperse processes. The experiments show, however, that the hypothesis put forward represents the actual relationships of the process of dissolution of colloids. The process is definitely heterogeneous, and, on account of the smallness of the particles of the solid phase and the Brownian movement, it is so modified that

it shows wide divergences from the process observed in the usual heterogeneous systems. J. F. S.

Metal Sols in Non-dissociating Liquids. I. Nickel in Toluene and Benzene. EMIL HATSCHEK and PERCY CYRIL LESLEY THORNE (*Proc. Roy. Soc.*, 1923, [*A*], **103**, 276—284).—Details are given of the preparation of very stable sols containing 1·0484 g. of nickel per litre of sol by decomposing nickel carbonyl in mixtures of benzene and toluene containing a small amount of caoutchouc as protective colloid. Sols so prepared can be concentrated considerably without coagulation by evaporating the dispersing medium. In an electric field, the particles of disperse phase move to and are deposited on both electrodes. In electric fields of different strengths, the amounts deposited on the electrodes are proportional to the first or a lower power of the potential gradient of the field. It is concluded, therefore, that positively and negatively charged particles are originally present in the sol, and that the charges do not originate owing to induction. The sol is coagulated by liquids, *e.g.*, acetone, which are not solvents for the protective colloid, and the coagulum is only very imperfectly peptised again by caoutchouc solvents such as toluene or benzene. J. S. G. T.

Sensitisation of the Process of Coagulation of Colloids. N. P. PESKOV (*Kolloid Z.*, 1923, **32**, 238—240).—When alcosols of arsenic trisulphide, platinum, and carbon are mixed with an equal volume of 0·063% solution of anthracene in ethyl alcohol and exposed at the ordinary temperature to the north light, coagulation of the sols is complete in six, five, and eight hours, respectively, whereas similar mixtures kept in the dark have not commenced to coagulate in seventeen days. The author explains the action as follows. The anthracene molecule, under the influence of light, loses an electron and thereby becomes positively charged. The positively charged anthracene molecule is adsorbed by the negatively charged colloid, and thereby brings about coagulation. J. F. S.

Borax Fusions with Gold Particles of Various Sizes and their Application to the Proof of von Smoluchowski's Coagulation Theory. A. EHRINGHAUS and R. WINTGEN (*Z. physikal. Chem.*, 1923, **104**, 301—314; cf. A., 1917, ii, 297).—Borax beads containing various quantities of gold from 0·1% to 0·0001% have been prepared by fusing together borax and auric chloride at 925° for periods varying from one minute to five hundred minutes. The beads show various colours, pale red, rose, violet, greyish-blue, mauve, light blue, blue, and deep blue, depending on the size of the suspended particles, but the authors were unable to produce colourless beads by rapid cooling of the melt, as is the case in the preparation of ruby glass. The number of particles per c.c. has been determined ultramicroscopically in all cases. It is shown that the gold particles increase in number with the concentration of gold, but decrease with the time of heating.

An increase in the concentration leads to larger particles more rapidly than a prolongation of the time of heating. The experimental results have been examined by means of an equation which is obtained by combining Smoluchowski's equation $\Sigma_\nu=\nu_0/(1+t/T)$ with Einstein's equation $D=H\theta/N\,.\,16\pi\eta\alpha$, where Σ_ν is the number of particles present at the time t, ν_0 the number of particles present originally, T the time of coagulation, which is given by $T=1/4\pi\,.\,DR\nu_0$, in which R is the radius of activity, D is the diffusion coefficient, H the gas constant $(83\cdot19\times10)^6$, θ the absolute temperature (1198°), N the Avogadro number $(60\cdot6\times10^{22})$, η the internal friction, and α the radius of the particles. The final equation has the form $1/\Sigma_\nu=1/\nu_0+(2H\theta R/3N\eta\alpha)t$. It is shown that the decrease in the number of particles with the time of heating is fully in keeping with von Smoluchowski's hypothesis. The gold particles combine together to form larger particles only when, in consequence of the Brownian movement, they are so close together as to be almost in contact. The results indicate that the von Smoluchowski hypothesis, which is true for hydrosols at the ordinary temperature, is also valid for fusions at 1000°. At 1000°, borax has a viscosity 3·38 at 890°, 13·61; and $d^{1000^\circ}=2\cdot04$.

J. F. S.

Adsorption. IV. Charge Reversal of some Colloids. N. R. Dhar and K. C. Sen (*J. Physical Chem.*, 1923, 27, 376—383; cf. this vol., ii, 58).—Freshly precipitated ferric hydroxide, when shaken with solutions of arsenious acid, boric acid, meconic acid, tartaric acid, and molybdic acid, passes into a negatively charged colloid. Transport experiments show that the hydroxides of copper, aluminium, chromium, zinc, and cobalt, peptised by alkali hydroxides, are negatively charged, due to the adsorption of hydroxyl-ions. The ammoniacal solutions of the hydroxides of copper, cadmium, zinc, and nickel contain negatively charged hydroxides of the respective metals, owing to the adsorption of the hydroxyl-ion from ammonium hydroxide. Positively charged arsenic sulphide sol may be obtained by the adsorption of thorium-ions by the negatively charged sol. In the presence of gelatin, as protective colloid, positively charged antimony sulphide sol may be obtained, due to the adsorption of thorium-, uranyl-, aluminium-, barium-, and hydrogen-ions by the negatively charged sol. A reversal of the charge of antimony sulphide sol in the presence of gelatin may be brought about by the addition of electrolytes such as thorium nitrate, uranium nitrate, potassium alum, barium chloride, hydrochloric acid, and ferric chloride. Reversal of the charge is primarily due to the amount of adsorption of ions. A univalent ion may, if it is highly adsorbed, reverse the sign of the charge on a colloid. The blue colour in ammoniacal solutions of cupric salts, Fehling's solution, a solution of cupric hydroxide in sodium hydroxide and in mixtures containing alkali, cupric salts, and glycerol or sugars, is most likely due to peptised negatively charged cupric hydroxide. Ferric hydroxide is found to be a good adsorbent for ferric salts. The adsorption of the basic portion

from salt solutions by hydrated manganese dioxide probably furnishes a reason for the acidity of soil. J. F. S.

The Question of Colloid Protection. N. P. Peskov (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 1—63).—The existing theories dealing with the protection and "astabilisation" of lyophobe colloids are reviewed and criticised. The erratic results recorded by a number of authors are mostly due to the fact that the solutions used by them are too concentrated; also to the fact that the protective colloid (gelatin) is not sufficiently free from electrolytes.

Working with a sol of arsenic trisulphide and specially purified gelatin in very dilute solution (A_2S_3 : 0·3, 0·05%; gelatin : 0·04, 0·02, and 0·004%), and using sodium chloride as the coagulating agent, the author shows that protection and astabilisation are separate and independent processes. Gelatin alone is unable to cause coagulation of colloids unless it is used in very concentrated solution containing very large particles; it is probable that in this case the lyophobe colloid is adsorbed by the large gelatin particles and these are then precipitated (Menz, A., 1909, i, 343). The protective action of gelatin is probably due to the formation of a film of gelatin particles around the particles of the lyophobe colloid, thus preventing their coalescence, in accordance with the view first put forward by Zsigmondy in 1901 (cf. "Kolloidchemie," Leipzig, 1922) and Freundlich ("Capillarchemie," Leipzig, 1909).

Billiter's electrical theory of "astabilisation" (A., 1904, ii, 18; 1905, ii, 305) is shown to be untenable for a number of reasons but chiefly because it presupposes that the particles of the lyophobe and the protective colloid must have opposite electrical charges, which is not always the case. It is suggested that the phenomenon is due to the interaction of the protective colloid with the traces of stabilisers always present in the particles of the lyophobe, either by the formation of a new system in which the stabiliser is partly adsorbed by the gelatin and thus removed from the lyophobe; or, conversely, by the precipitating action of the stabiliser on the gelatin which diminishes the concentration of the latter. It appears possible, however, that, concurrently with this main factor, the neutralisation of the electrical charges of the lyophobe particles by ions of an electrolyte may be accelerated by the adsorption of the latter by the protective colloid.

G. A. R. K.

The Question of Colloid Protection. The Phenomenon of "Reverse" Protection. Nikolai Petrovitsch Peskov and V. V. Tretiakov (*J. Russ. Phys. Chem. Soc.*, 1917—1918, **49**, 547—566; cf. preceding abstract).—Colloidal solutions of albumin purified by prolonged dialysis are readily coagulated on heating, although the presence of even minute quantities of electrolytes prevents coagulation (Pauli, A., 1907, i, 803; 1909, i, 618; 1913, ii, 558); these therefore act as "stabilisers." Now the phenomenon of "astabilisation" of lyophobe colloids by the addition of small quantities of a lyophile colloid (gelatin) was explained by one of the authors (preceding abstract) by the transference of the

"stabiliser" to the particles of the lyophile colloid. It would therefore be expected that an unstable albumin solution might be able to acquire the required stabiliser on mixing with a colloidal solution of a lyophobe substance, by depriving the particles of the latter of the stabiliser adsorbed by them. This was found to be the case, and hydrosols of gold, silver, platinum, stannic acid, and ferric hydroxide were found to protect the albumin solution from heat coagulation, although they were very carefully freed from electrolytes. It is an interesting fact that such a protected solution was coagulated if, after boiling and cooling, it was subjected to dialysis. This is taken to indicate that, although no coagulation occurs on boiling the protected solution, the albumin undergoes some chemical change, and is no longer able to retain the stabilising substances; this is confirmed by the fact that coagulation is also caused by adding some fresh albumin solution to the boiled protected solution; the loosely held stabiliser is removed by the fresh albumin. The phenomenon of reverse protection is also shown to occur in solutions of gelatin, which can be made temporarily resistant to the coagulating action of tannic acid by the addition of metallic sols. G. A. R. K.

Protective Colloids. V. The Seed of *Plantago psyllium*, L., as Protective Colloid. II. Colloidal Selenium. A. Gutbier, J. Huber, and P. Eckert (*Kolloid Z.*, 1923, **32**, 255—262; cf. A., 1916, ii, 556).—Very stable solutions of colloidal selenium may be prepared by reducing selenium dioxide in the presence of the chloroform-water extract of the seeds of *Plantago psyllium*, L., by hydrazine hydrate at the ordinary temperature. Systems coloured yellow, yellowish-red, vermilion, blood-red, and bluish-red can be obtained, but if the faintest blue flickering is observed in the sols, coagulation follows almost immediately. Evaporation of the colloidal solutions gives reversible residues containing up to 65% of selenium. J. F. S.

Protective Colloids. V. Seeds of *Plantago psyllium*, L., as Protective Colloid. III. Colloidal Tellurium. K. Gutbier, J. Huber, and P. Eckert (*Kolloid Z.*, 1923, **32**, 329—330; cf. preceding abstract).—The extract of the seeds of *Plantago psyllium*, L., has been examined as a protective colloid for colloidal tellurium. It is shown that highly dialysed sols of tellurium prepared by the action of hydrazine hydrate on telluric acid in the presence of the extract are extremely stable, but the amount of the protective colloid ought not to exceed 0·3%. The colloidal tellurium prepared under the above-named conditions is negatively charged. Concentration of the sol solutions furnishes solid residues containing up to 30% of tellurium, but these are completely irreversible except in those cases where the tellurium concentration is very small. J. F. S.

Protective Colloids. III. Gum Tragacanth as Protective Colloid. II. Colloidal Silver. A. Gutbier and W. Wüterich (*Kolloid Z.*, 1923, **32**, 331—333; cf. *ibid.*, 1916, **18**, 145).—Silver

nitrate may be reduced to colloidal silver by suspensions of gum tragacanth in ammoniacal solutions, the colloidal system being coloured various shades of brown. On keeping, the solutions become coated with a thin silver mirror and deposit a brown reversible precipitate. The colloidal system is not very stable toward electrolytes; $0.1N$-ammonium chloride produces complete coagulation in twenty-four hours. Evaporation gives reversible residues which contain up to 79·24% of silver. J. F. S.

Flame as an Example of a Stationary Disperse System. P. P. VON WEIMARN (*Kolloid Z.*, 1923, **32**, 253—255).—A theoretical note in which flame is discussed as a disperse system. J. F. S.

Determination of the Distribution of Size of Particles in Disperse Systems. THE SVEDBERG and HERMAN RINDE (*J. Amer. Chem. Soc.*, 1923, **45**, 943—954).—The principles for the determination of the distribution of size of particles in a disperse system are discussed, and an improved form of Odén's method (A., 1916, ii, 301) is described. This makes use of a self-recording sedimentation balance, which permits of the recording of quantities as small as 0·02 g. with an accuracy of 0·00001 g. This method depends on the compensation of the increasing weight of sediment by means of an electric current passing through a coil acting on an iron cylinder, recorded on a sensitive recording milliammeter. The compensation apparatus works automatically by means of a system of relays and a drum resistance rotated by a motor. From the relation between time and current, the sedimentation curve can be found, and from this curve the distribution curve can be calculated. To illustrate the process, the sedimentation and distribution curves of a mercury hydrosol and a gold hydrosol have been determined and are given in the paper. A method is described for determining the distribution of size of particles, depending on the variation of concentration with height in a sedimenting system. As an example, a gold hydrosol was studied, the concentration at different heights being measured by means of the light absorption. The theory for the development of an analogous method depending on the use of centrifugal force has been discussed. J. F. S.

The Validity of the Partition Law in the Equilibrium between Mixed Crystals and their Solutions. G. MEYER (*Rec. trav. chim.*, 1923, **42**, 301—316).—A study of the potassium chromate–potassium sulphate–water, lead chloride–lead bromide–water and *p*-dichlorobenzene–*p*-dibromobenzene–water systems shows that in the two former cases the partition law probably holds, and in the latter it can be demonstrated with certainty. The lack of agreement of the author's observations in the latter case with those of Würfel (*Thesis*, Marburg, 1896) is ascribed to the non-attainment of equilibrium in that worker's experiments. The validity of the results obtained is dependent on the assumption that the substances used have the same molecular constitution in solution as in the solid phase. H. J. E.

Two Cases of Binary Eutectic Cycles. ALEXEI MICHAILOVITSCH VASILIEV (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 428—431).—Flavitski's rule (A., 1906, ii, 152) for cycles of three binary fusion diagrams is shown to hold for the systems antimony chloride–α-nitronaphthalene, and antimony chloride–β-chloronaphthalene. In both these systems, compound formation occurs, but it is also possible to realise the unstable eutectic points of the components. Each system may therefore be regarded as being composed of three systems, *e.g.*, antimony chloride–compound, compound–α-nitronaphthalene, and α-nitronaphthalene–antimony chloride. R. T.

The Probable Composition of the Eutectics of some Volatile Substances. ALEXEI M. VASILIEV (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 432—441).—Flavitski's rule (A., 1906, ii, 152) is applied to sixteen binary systems of volatile components, namely, methyl ether and methyl alcohol with sulphur dioxide, hydrogen chloride, methyl chloride, carbon dioxide, hydrogen sulphide, and ammonia; methyl alcohol with water; hydrogen chloride with methyl chloride and sulphur dioxide; and ammonia with water (Baume and co-workers, A., 1914, ii, 446, 635, 636). The compositions of the eutectic mixtures calculated on the above rule in most cases agree within 6 mol.% with those obtained by Baume and his collaborators.
R. T.

Rhythmic Precipitation Processes. K. NOTBOOM (*Kolloid Z.*, 1923, **32**, 247—252).—The author describes a new method for the production of Liesegang rings which allows the formation of the rings being followed microscopically. Observations are made which, in the author's opinion, supports Ostwald's hypothesis of the formation of rhythmic precipitates, namely, that the precipitates are due to a metastable boundary of the supersaturated solution ("Lehrbuch allg. Chemie," 1899, II, 2, 778). J. F. S.

Rhythmic Banded Films of Precipitates on the Surface of Liquids. I. A. JANEK (*Kolloid Z.*, 1923, **32**, 252—253).—A banded film precipitate may be prepared by pouring a solution of 1·0 g. of gelatin and 0·21 g. of potassium dichromate in 30 c.c. of water on to a glass plate so that a thin film is formed. This is allowed to solidify and then a small crystal of silver nitrate is placed on the film and moistened with a drop of water. Bands 0·08—0·15 mm. broad are produced. J. F. S.

Action of Heat on the Formation of Precipitates in Jellies. R. ED. LIESEGANG (*Kolloid Z.*, 1923, **32**, 263—264).—Hatschek has shown (*Proc. Roy. Soc.*, 1921, [*A*], **99**, 496) that light has a marked influence in the rhythmic precipitation of lead acetate by potassium dichromate. The author now shows that when silver nitrate is allowed to diffuse into dialysed gelatin solutions in the dark a marked turbidity is produced, but when the turbidity is exposed to electric light for an hour and then preserved in the dark for twenty-four hours it is found to have disappeared. This is not due, as the experiment would appear to indicate, to the

effect of light, but to the fact that the lighted room was 10° warmer than the dark room. J. F. S.

The Propagation of the Explosion-Wave. I. Hydrogen and Carbon Monoxide Mixtures. HAROLD BAILY DIXON and NOEL STANLEY WALLS (T., 1923, **123**, 1025—1037).

The Combustion of Complex Gaseous Mixtures. II. Mixtures of Carbon Monoxide and Hydrogen with Air. WILLIAM PAYMAN and RICHARD VERNON WHEELER (T., 1923, **123**, 1251—1259).

The So-called Pre-pressure Interval in Gaseous Explosions. JOHN DAVID MORGAN (T., 1923, **123**, 1304—1308).

The Energy of Activation in Heterogeneous Gas Reactions with Relation to the Thermal Decomposition of Formic Acid Vapour. CYRIL NORMAN HINSHELWOOD and BRYAN TOPLEY (T., 1923, **123**, 1014—1025).

The Velocity of Reaction in Mixed Solvents. V. *a*. The Velocity of Formation of Quaternary Ammonium Salts. *b*. The Study of an Intramolecular Change. JOHN DEXTER, HAMILTON McCOMBIE, and HAROLD ARCHIBALD SCARBOROUGH (T., 1923, **123**, 1229—1241).

The Speed of Chemical Reaction through a Solid. C. D. NIVEN (*Chem. News*, 1923, **126**, 183—186).—Making the assumptions that the time taken to complete the chemical reaction within a small area in the solid is proportional to the distance of the area from the surface, inversely proportional to the average width of passage, and proportional to the amount of chemical reagent required, calculations are made for the relative speeds of penetration into cylinders, and spheres of varying dimensions, and these checked by experimental measurements on the speed of penetration of casein by formaldehyde. In view of the difficulties in arriving at the exact end-point, the agreement between theory and experimental is satisfactory. W. E. G.

The Mode of Reaction of Highly Insoluble or Undissociated Salts. BENJAMIN S. NEUHAUSEN (*Science*, 1923, **57**, 26).—In support of Haber's contention (A., 1904, ii, 607, 808) that molecules and complex ions take part in reactions between highly insoluble or slightly dissociated substances, attention is directed to the rapid dissolution of mercuric sulphide by a solution of iodine in aqueous potassium iodide and to the precipitation of mercuric sulphide by addition of sodium sulphide to a solution containing the mercuricyanide-ion. In the latter case, precipitation takes place rapidly in a solution through which, it may be calculated, one mercury-ion flashes at minimum intervals of ten seconds (cf. Smith, A., 1922, ii, 626). A. A. E.

Hydration of Meta- and Pyro-phosphoric Acids. LEOPOLD PESSEL (*Monatsh.*, 1923, **43**, 601—614).—The velocity of hydration

of metaphosphoric acid in aqueous solution is increased by addition of hydrochloric acid, the velocity being roughly proportional to the hydrion concentration. The velocity constant in half the experiments increased with time, probably owing to the presence of polymerised metaphosphoric acids. Pyrophosphoric acid is not formed as an intermediate compound in this process. As stated by Sabatier (A., 1888, 404; 1889, 671), the conversion of sodium metaphosphate into orthophosphate is accelerated by adding excess of alkali, in rough proportion, to the excess added.

The hydration of pyrophosphoric acid, which may be prepared in a few days from the lead salt (cf. Giran, A., 1903, ii, 139), is also accelerated by adding hydrion, the effect again being only roughly proportional to the concentration of the latter, however. The rate of hydration is smaller than in the case of the meta-acid (cf. Montemartini and Egidi, A., 1902, ii, 451). Mixtures of pyro-acid and hydrochloric acid show an abnormally low electrical conductivity, probably owing to the formation of a feebly dissociating compound between the two acids.

Sodium pyrophosphate does not change into the ortho-salt during six months in aqueous solution at 25°, even in the presence of alkali. E. E. T.

Mechanism of Catalytic Reactions. Decomposition of Hydrogen Peroxide by Metallic Oxides. J. Clarens (*Bull. Soc. chim.*, 1923, [iv], **33**, 280—293).—A study was made of the catalytic decomposition of hydrogen peroxide in the presence of metallic oxides or hydrated oxides precipitated in the peroxide solution by the addition of sodium hydroxide to the corresponding metallic salt. Under these conditions, the decomposition was essentially a physical phenomenon, depending primarily on the physical state of the catalyst. The possibility of a chemical type of catalysis was excluded by reason of the fact that the decomposition was retarded or altogether inhibited when the metallic oxide was in colloidal or actual solution. Thus in the case of manganese, a colloidal manganese dioxide is first formed, and exactly coincident with its flocculation there is a considerable increase in the velocity of the peroxide decomposition. Conversely, in the case of lead, the peroxide precipitated by the addition of the first few drops of sodium hydroxide to a mixture of hydrogen peroxide and a solution of a lead salt, causes a decomposition which ceases on the addition of a further quantity of sodium hydroxide sufficient to redissolve the whole of the precipitated lead peroxide. The stabilisation of hydrogen peroxide by acids is thus apparently due to their solvent action on traces of metallic oxides which would otherwise cause slow decomposition. The decomposition of hydrogen peroxide being the result of its adsorption by the catalyst, and the amount adsorbed being a variable fraction of the total quantity present, the reaction only becomes unimolecular at the limit at which all that present is adsorbed. The activity of the catalyst does not depend only on its mass and physical state, but also on the concentration of the hydrogen peroxide on which it acts. G. F. M.

The Contact Action of Charcoal in Reactions of Oxidation. ANTONI GRIGOREVICH DOROSCHEVSKI and G. S. PAVLOV (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 169—175).—Sulphur is mixed with birch or sugar charcoal containing a little sodium carbonate, and the mixture heated at 100°. Moist air is then passed over it for some time, and the mixture is analysed for sulphuric acid, the yields of which were variable, and small in quantity. Charcoal is saturated with hydrogen sulphide, aqueous sodium carbonate is added, the hydrogen sulphide removed, and the charcoal carefully dried. Examination of the product shows that a certain amount of the hydrogen sulphide has decomposed, liberating sulphur, the sulphur content being such that from 1 g. of the mixture 0·5376 g. of barium sulphate could be obtained. A portion of the mixture is then treated as before, and it is found that after thirty hours no further oxidation takes place, and that 0·1296 g. of barium sulphate can be obtained per 1 g. of mixture. This amount corresponds with the production of an amount of sulphuric acid just sufficient to neutralise the alkali present, and if more of the latter is added, and the process repeated, further sulphur can be oxidised. Birch or sugar charcoal is shown to be a quite efficient catalyst for the oxidation of sulphur dioxide to sulphur trioxide. R. T.

Influence of Temperature, Pressure, and Supporting Material for the Catalyst on the Adsorption of Gases by Nickel. ALFRED WILLIAM GAUGER and HUGH S. TAYLOR (*J. Amer. Chem. Soc.*, 1923, **45**, 920—928).—The adsorption of hydrogen by nickel has been investigated at various temperatures between 25° and 305°, with the nickel supported on diatomaceous earth, diatomite brick, or entirely unsupported. Adsorption isotherms of hydrogen on nickel have been constructed, using nitrogen as reference gas. A definite saturation capacity of nickel for hydrogen exists which depends on the temperature. From the variation of the saturation pressure with temperature, the heat of adsorption of hydrogen on nickel has been calculated to be approximately 2,500 cal. Other methods of calculation give a value of 12,000 cal. The effect of using an inert material for catalyst support has been found to increase greatly the adsorptive capacity per gram of nickel and to yield a catalyst which will withstand much more severe heat treatment without diminution of its adsorbing power.

J. F. S.

Velocity of Catalytic Reactions. J. ZALKIND (*Z. physikal. Chem.*, 1923, **104**, 177—191).—The rate of reaction between hydrogen and solutions of $\beta\epsilon$-dimethyl-Δ^{γ}-butinene-$\beta\epsilon$-diol, $\alpha\alpha\delta\delta$-tetraphenylbutinene-$\alpha\delta$-diol, $\gamma\zeta$-dimethyl-Δ^{δ}-octinene-$\gamma\zeta$-diol, and phenylacetylene in ethyl alcohol has been measured in the presence of either palladium or platinum black at the ordinary temperature. The results show that the addition of hydrogen by acetylene derivatives does not in general follow the equation for a reaction of the first order and that the mechanism of the reaction is complicated as in the case of reactions catalysed by biological catalysts. In both cases, the formation of an intermediate product must be assumed,

which may be a definite compound or an adsorption complex. Probably in heterogeneous catalysis an adsorption constitutes the first stage and this is followed by the formation of an unstable chemical compound; otherwise it would be difficult to understand why the hydrogenation of different types of acetylene derivatives takes place so differently. The chemical nature of the catalyst plays an important *rôle* in the reaction, palladium having a markedy different action from platinum. J. F. S.

Problem of Negative Catalysis. I. HUGH S. TAYLOR (*J. Physical Chem.*, 1923, **27**, 322—341).—A theoretical paper in which a new hypothesis of negative catalysis is proposed to supplement the hypotheses hitherto held to explain the mechanism of special cases. The present hypothesis accounts for the inhibitory power of the negative catalyst by assuming an interaction between one of the reacting substances and the inhibitor, with the formation of a molecular compound, as an alternative to reaction between two or more of the reacting substances. The extent of the inhibition is determined by the degree and the velocity of compound formation. It is shown that the inhibitory power of water and the alkali sulphates in the decomposition of oxalic acid in solutions of sulphuric acid, that of water in various reactions in sulphuric acid and acetone solutions, and that of a large number of organic and inorganic compounds of widely varying character in the inhibition of autoxidation processes, can be readily explained on the basis of the present hypothesis. The experimental evidence obtained in all these cases is readily explained by the hypothesis, and various predictions have been made on this basis which have already been to some extent verified. The whole subject of negative catalysis is discussed, and many references to the literature of the subject are included in the paper. J. F. S.

Change of Properties of Substances on Drying. II. HERBERT BRERETON BAKER (T., 1923, **123**, 1223—1224).

A Static or Dynamic Atom? NORMAN R. CAMPBELL (*Nature*, 1923, **111**, 569).—It is pointed out that if the sharing of an electron means the sharing of an orbit, compounds being formed when some of the electronic orbits surround both nuclei, the Lewis-Langmuir theory can be expressed in terms of Bohr's conceptions, although the question whether such shared orbits are possible is one for the quantum theory to decide. A. A. E.

The Spectrum of the Semi-circular Helium Model. H. O. NEWBOULT (*Phil. Mag.*, 1923, [vi], **45**, 1085—1087).—A theoretical examination of the Langmuir model of the helium atom (cf. A., 1921, ii, 656). Since the ordinary Sommerfeld-Wilson quantum condition when applied to this model gives a negative value for the ionisation potential, Langmuir suggested that the maximum angular momentum of a single electron be set equal to $h/2\pi$, and deduced a value for the ionisation potential which agreed with the experimental value. This quantum condition is

shown to lead to a spectrum for the helium atom which does not agree with that of any known series. W. E. G.

The Crossed-orbit Model of Helium, its Ionisation Potential and Lyman Series. L. SILBERSTEIN (*Nature*, 1923, **111**, 567).—Mathematical. The ionisation potential is calculated for Bohr's model to be 24·35 volts, in close agreement with Lyman's latest observed value, 24·5 volts. A formula has been developed which, regardless of its significance or deduction, gives the correct ionisation potential for a number of simple rational values of $-\cos i$. A. A. E.

The Dimensions of Atomic Nuclei, and the α-, H⁺, β-, and γ-Rays. MAXIMILLIAN CAMILLO NEUBERGER (*Ann. Physik*, 1923, **70**, 139—152).—A theoretical paper in which the upper and lower limits for the radii of the atomic nuclei are calculated. From the ranges of H^+ rays (Rutherford and Chadwick, A., 1921, ii, 293), and the ranges of α- and β-rays of radioactive elements, deductions are made with regard to the nuclear dimensions of all the elements. The radioactive isotopes possess widely different nuclear radii, and, on the other hand, elements with different atomic numbers give almost identical values for the lower limit of the radius of the nucleus. Periodic changes in the atomic dimensions of the elements in the radium, actinium, and thorium families are found as the atomic number decreases. Thus from uranium I to radium-*A* a decrease in the radius takes place, followed by a large increase at radium-*C*, a rapid fall at radium-*C'*, and finally a rise to radium-*F*. This periodicity shows little resemblance to the periodic course of the atomic volume curve of these elements. W. E. G.

An Explanation of the Theory of the Rotation of the Atomic Nucleus. I. HERBERT HENSTOCK (*Chem. News*, 1923, **126**, 262—266).—The theory advanced in a previous paper is further elaborated (cf. this vol., ii, 233). Some of the edges of the cubic atom of the Lewis-Langmuir theory will be negatively and some positively charged. Union between atoms will take place through juxtaposition of oppositely charged edges. This will lead to opposite orientation of the nuclei of adjacent atoms, resulting in alternate polarity. Double and treble bonds between carbon atoms are considered. E. H. R.

Experiments with a Model to Illustrate the Combination of Two Atoms consisting of Magnetons round a Positive Nucleus. A. P. LAURIE (*Proc. Roy. Soc. Edin.*, 1923, **43**, 72—84).—A mechanical model designed to investigate the probable behaviour and disposition of magnetons in a magnetic field is described. The arrangements of magnetons and nucleus in molecules of oxygen, water, marsh gas, acetylene, ethylene, ethane, benzene, and carbon chain compounds are detailed, and it is suggested that chemical combination consists, in the first place, of addition. Thus in the combination of hydrogen and oxygen to form water, two molecules of hydrogen attach themselves to a

molecule of oxygen by means of secondary valencies to form H_4O_2, which tends to cleave into two groups H_2O, this rearrangement reducing the total electrostatic and magnetic potential energy of the system. J. S. G. T.

The Quantum Theory and Isotopes. J. W. NICHOLSON (*Phil. Mag.*, 1923, [vi], 45, 801—817).—A theoretical paper dealing with the quantum theory of spectra and atomic structure. Since the energy of an atom is independent of the system of co-ordinates used in its calculation, the pendulum paths of the electrons should yield the same values as those from other orbits. The energy of a hydrogen atom in which the electron is traversing a pendulum path about the nucleus is shown to be given by $W=2\pi^2me^4\nu^2/n^2h^2$. It is suggested that in the nucleus an interpenetration of the electric charges may possibly occur. A double mesh structure of the ether would admit of this possibility, so that two strain systems in the same region would not annihilate each other and might pass through each other. Assuming that the quantising relation can be applied to the nucleus, it is shown that the possible hydrogen isotope, the "inverted Bohr model" of Lenz, in which two nuclei rotate symmetrically around an electron, has a spectrum which shows detectable differences from the ordinary hydrogen spectrum. The differences between the spectra of the lithium isotopes should be much smaller than those found recently by McLennan and ascribed to these isotopes. The effect for lead is comparable with that already known to occur. From a study of the structure of ionised helium, it is considered that the hypothesis of nuclei made entirely of hydrogen is unsound. W. E. G.

The Separation of Elements and Isotopes by Diffusion. ERNST MURMANN (*Oesterr. Chem. Ztg.*, 1923, 26, 14—15).—The diffusion method has been applied to uranium, chlorine, and lithium, and in no case was any separation effected, although the same method was successful when employed in the separation of nickel from cobalt. Several attempts were made to isolate the isotopes of uranium by diffusion, fractionation, and precipitation. Thus it was precipitated many hundreds of times as tetroxide, crystallised, and fractionally precipitated in the form of its double salts, and uranyl nitrate was fractionated by a diffusion process. Sodium and lithium chlorides were also subjected to diffusion processes, but in no case was any separation observed within the experimental error of the analyses. It is considered that ionic mobility is dependent only on the atomic volume, and not on the atomic weight. This provides an explanation of the differences between the behaviour of mixtures of elements and of isotopes during diffusion processes. W. E. G.

Valency. WILLIAM R. FIELDING (*Chem. News*, 1923, 126, 177—180, 193—197, 209—214, 226—229).—A discussion of the variability of valency. The effect of temperature on polymerisation and on valency is considered in detail. W. E. G.

Supposed Relationships between Atomic Constants and the Valency Number of the Atoms. WALTER HÜCKEL (*Z. physikal. Chem.*, 1923, **104**, 262—268).—A theoretical paper in which the author shows that the relationship between atomic constants and the physical properties (heat of combustion, molecular volume, molecular refraction, molecular cohesion, and other additive properties) as put forward by Le Bas (P., 1907, **22**, 322; A., 1918, ii, 667), Traube (A., 1907, i, 145; ii, 205), and Walden (A., 1909, ii, 119) are without meaning. They do not follow from the experimental data, but are due to the use of an inexact method of calculation. It is shown that the function φ=*additive molecular property/sum of the valencies* is generally, within wide limits, almost independent of the numerical relationships of the atomic constants of the particular property, just as it is almost independent of the chemical nature of the compound. If φ should prove to be rigidly constant, then it would follow that the atomic constants are proportional to the valency number, but an approximate constancy of φ does not allow of any definite conclusion being drawn, not even the statement of an approximate rule. Consequently, the relationships, quoted in the literature, between atomic volume, atomic refraction, and atomic cohesion, on the one hand, and the valency number, on the other, which are based entirely on an approximately constant value of φ, do not in reality exist. J. F. S.

Other Factors Influencing Co-ordination. T. MARTIN LOWRY (*Chemistry and Industry*, 1923, **42**, 412—415).—In continuation of previous work (this vol., ii, 313), the author considers the transfer of electric charges and ring formation, respectively, as influencing co-ordination. The sharing of electrons between atoms which accompanies co-ordination causes a transfer from the radicles to the metal, and these latter components also become united by covalencies. The effects are illustrated by reference to methylethylaniline oxide, the chloroplatinates, the cobaltammines, and the metallic carbonyls. Co-ordination can be effected, often under very adverse conditions, by making the co-ordinated groups part of a conjugated system. A conjugated ring-system containing three positively-charged and three negatively-charged atoms, as in benzene, is particularly favourable to co-ordination.

J. S. G. T.

Apparatus for the Measurement of the Rate of Flow of Gases. V. ARKADIEV (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 210—220).—An apparatus for measuring the rate of flow of gases, for which the name rheometer is proposed, is described. The gas is made to pass through a narrow tube, the ends of which are in connexion with the limbs of a manometer. The difference of pressure recorded in the manometer is then a measure of the speed at which the gas passes through the tube. Instead of this tube, a diaphragm pierced with a small aperture may be used. An arrangement is also described for regulating the rate of flow of gases, this consisting of a diaphragm provided with an aperture, the rate of flow being proportional, with any given pressure, to the diameter

of the aperture. A rheometer constructed on a different principle is described, for use with higher velocities, in which the velocity of the gas is proportional to the height to which a small ebonite floater in a glass tube can be raised by it. Such an apparatus may also be used for the measurement of quantities of gases, by passing them at a known speed, for a definite interval of time, through a tube of known diameter, and its possible use in reactions involving gaseous combination is pointed out. R. T.

An Apparatus for Continuous Extraction with Boiling Solvents. O. P. A. H. Schaap (*Pharm. Weekblad,* 1923, **60**, 375—376).—A slight modification of the apparatus used for extraction with boiling chloroform (A., 1922, ii, 797) to render it safe for use with low-boiling, inflammable solvents. S. I. L.

Chemistry in Mediæval Islam. E. J. Holmyard (*Chemistry and Industry,* 1923, **42**, 387—390).—In emphasising the importance of more detailed study of the Arabic chemical manuscripts, the author briefly discusses the position of certain individuals, and maintains that the first successful efforts to place chemistry on a scientific basis and apply scientific method originated in Islam. A. A. E.

Inorganic Chemistry.

Active Hydrogen by the Action of an Acid on a Metal. A. C. Grubb (*Nature,* 1923, **111**, 600; cf. Wendt and Landauer, A., 1920, ii, 425).—Active hydrogen can be readily detected even in presence of moisture by direct combination with nitrogen to yield ammonia. When hydrochloric or sulphuric acid is dropped on to magnesium suspended so as to avoid immersion, and the hydrogen rapidly evolved is passed through a glass-wool plug, its activity is demonstrated by the formation of ammonia with pure nitrogen. It is concluded that the activity is not due to ions or to atomic gas. Langmuir (A., 1912, ii, 1162) has shown that monatomic hydrogen does not react with nitrogen to form ammonia, yet if nitrogen is allowed to impinge on the surface of magnesium at which evolution of hydrogen is taking place, a maximum quantity of ammonia is formed. Moreover, slow evolution of hydrogen, with subsequent passage through glass wool and admixture with nitrogen, does not result in the production of ammonia. The life of the active gas, about two minutes, is in agreement with that of triatomic hydrogen formed by other methods. The results are considered to substantiate the view of Wendt and Landauer (A., 1922, ii, 369) that triatomic hydrogen should be produced wherever atomic hydrogen is evolved. A. A. E.

Active Hydrogen by Electrolysis. A. C. Grubb (*Nature,* 1923, **111**, 671).—By using a method corresponding with that for

the electrolytic production of ozone, namely, by electrolysis of a solution of sulphuric acid with a high current density at the cathode, active hydrogen is produced, and will combine with pure nitrogen to form ammonia. The ozone form of hydrogen is also produced by the electrolysis of a solution of potassium hydroxide, when a high cathode current density is employed. A. A. E.

The Aëration of Quiescent Columns of Distilled Water and of Solutions of Sodium Chloride. W. E. ADENEY, A. G. G. LEONARD, and A. RICHARDSON (*Phil. Mag.*, 1923, [vi], **45**, 835—845).—The aëration of water under natural conditions is effected by mixing of the exposed layer with the unexposed portions of the water to depths of at least 10 feet. The mixing is brought about by the downward "streaming" of the constantly changing layer of water exposed to the air. This process is more rapid in salt than in fresh water. The rate of "streaming" is dependent on the rate of cooling and concentration of the surface layers, which is brought about by evaporation, and is more rapid at temperatures above 10° than below it. A 1% solution of sodium chloride gives the optimum conditions for the streaming process.
W. E. G.

The Formation of Hydrogen Peroxide during the Combustion of Hydrogen. MAX HAUSER (*Ber.*, 1923, **56**, [*B*], 888—894).—The combustion of hydrogen in oxygen has been shown to be a termolecular reaction in accordance with the equation $2H_2+O_2=2H_2O$, which occurs mainly at the walls of the containing vessel, but evidence has also been adduced (cf. von Wartenberg and Sieg, A., 1921, ii, 107) that hydrogen peroxide is intermediately produced and that changes represented by the appended equations take place: $H_2+O_2=H_2O_2$. $H_2O_2=H_2O+\frac{1}{2}O_2$. $H_2+\frac{1}{2}O_2=H_2O$. Attempts are now described to catalyse the first reaction to such an extent that it occurs at temperatures below that at which rapid decomposition of hydrogen peroxide sets in, and also to effect the reaction in such a manner that the products are very rapidly cooled and thus shielded from speedy decomposition. The results, however, are negative.

Inexplosive mixtures of hydrogen and oxygen containing a large excess of one or other gas are passed over porous earthenware impregnated with platinum, palladium, silver, copper, iron, cobalt, or nickel at temperatures varying between 100° and 500°. Copper or iron-wire gauze, glass fragments, or glass wool are also suitable catalyst carriers, but asbestos, platinised or palladised asbestos, pumice, or aluminium powder causes immediate decomposition of hydrogen peroxide. Combustion of the hydrogen occurs invariably, but the presence of hydrogen peroxide in the condensates could not be detected in any instance by means of titanic acid with which a concentration of 0·00001% H_2O_2 can be readily detected. It appears probable that the contact agent catalyses both the formation and decomposition of hydrogen peroxide (cf. Hofmann, A., 1922, ii, 490).

In a second series of experiments, the rapid heating and cooling

of the mixture of gases are effected by its momentary adiabatic compression in a steel cylinder containing a small quantity of water. Partial combustion invariably occurs, but the presence of hydrogen peroxide in the water could not be detected in any instance. The supposition that the heating is sufficiently prolonged to cause the decomposition of any hydrogen peroxide which is produced is not in accord with the known properties of the substance, and under these conditions it appears probable that the formation of water is a true termolecular change.

Repetition of the experiments of von Wartenberg and Sieg on the passage of mixtures of hydrogen and oxygen through a "hot-cold" tube (*loc. cit.*) have confirmed the results of these workers and shown that the yields of hydrogen peroxide are not appreciably affected by change in the chemical nature of the walls of the tube. The effect of the introduction of quartz, copper gauze, platinum foil, and silver foil into the tube is described, but does not appear to be simply explicable. The comparatively large production of hydrogen peroxide in the "hot-cold" tube is due to the catalytic action of the glowing wall; the high temperature of the latter involves a low adsorptive power, and the hydrogen peroxide is therefore shielded from immediate reduction unless the hydrogen is in great excess. H. W.

The Solubility of Chlorine in Water. V. ARKADIEV (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 205—209).—The solubility of chlorine at various temperatures and pressures is calculated from a formula deduced by Jakovkin (*ibid.*, 1900, 32, 673), namely, $x=r+7\cdot94\sqrt[3]{kr(1+\omega t/c)^2}$, where x is the ratio of the concentration, in millimoles per litre, of chlorine in the water to that in the atmosphere, r the ratio of unhydrolysed to total chlorine in the water, k the hydrolysis constant for chlorine in water, ω the coefficient of expansion of chlorine, $=0\cdot00371$, t the temperature, and c the volume concentration of chlorine in the atmosphere. The values thus obtained agree satisfactorily with those obtained experimentally.

R. T.

Solubility of Selenium in Alkali Hydroxides. G. CALCAGNI (*Gazzetta*, 1923, **53**, i, 114—119; cf. A., 1921, ii, 195).—Powdered selenium dissolves readily in the cold in 66% sodium or potassium hydroxide solution, more slowly in saturated barium hydroxide solution on a boiling water-bath, and only slowly and in very small proportion in ammonia solution (d 0·888). The solutions thus obtained contain selenides, selenites, and, possibly, a compound analogous to the thiosulphate, formed by the action of atmospheric oxygen on the selenides; it may be, also, that a small part of the selenium is present as such in the solutions. The reactions taking place are gradual and highly complicated, the first products consisting of selenides, which subsequently undergo transformation into polyselenides and selenites. The solutions formed are at first brown, but are gradually decolorised by the combined action of the oxygen and carbon dioxide of the air.

T. H. P.

Preparation of Hydrazine by Raschig's Method. REGINALD ARTHUR JOYNER (T., 1923, **123**, 1114—1121).

Reactions of Chlorites with Salts of Hydrazine and of Hydroxylamine. GIORGIO RENATO LEVI (*Gazzetta*, 1923, **53**, i, 105—108).—Treatment of a solution of freshly prepared alkali chlorite with commercial hydrazine hydrate results in immediate liberation of nitrogen and gradual heating of the liquid, whereas if pure hydrazine hydrate is used neither evolution of gas nor heating is observed. The decomposition is thus accelerated by the presence of extraneous substances, and in neutral boiling solution proceeds quantitatively according to the equation $N_2H_4,2HCl+NaClO_2=N_2+NaCl+2H_2O+2HCl$. The decomposition is slower in alkaline solution, and is accelerated by traces of iron or copper salt.

Hydrazine chlorite, $N_2H_4,HClO_2$, obtained as white crystals by the reaction $(N_2H_4)_2,H_2SO_4+Ba(ClO_2)_2=BaSO_4+2N_2H_4,HClO_2$, inflames spontaneously when dry.

The reaction of hydroxylamine hydrochloride (1 mol.) with a neutral solution of a chlorite (1 mol.), expressed by the equation $NH_2{\cdot}OH,HCl+NaClO_2=NaCl+Cl+NO+2H_2O$, occurs rapidly and with development of a considerable amount of heat. With excess of the hydroxylamine salt, however, the reaction takes place in accordance with the equation $2NH_2{\cdot}OH,HCl+NaClO_2=NaCl+N_2O+3H_2O+2HCl$. T. H. P.

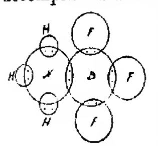
The Preparation of Hydrazine Sulphate and Sodium Azide. B. P. ORELKIN, V. G. CHLOPIN, and I. I. TSCHERNIAEV (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 82—87).—The authors give full details for the preparation of hydrazine sulphate by Raschig's method (A., 1908, ii, 1029), and of sodium azide by Thiele's method (A., 1908, ii, 940). The hydrazine hydrate for the latter process is prepared by means of alcoholic sodium hydroxide instead of by the sodium methoxide used by Thiele. G. A. R. K.

The Discovery of Red Phosphorus. R. WINDERLICH (*Chem. Ztg.*, 1923, **47**, 297).—In the year 1813, Vogel published a paper on the action of sunlight on phosphorus (*Schweigger's J.*, 1813, **7**, 95—121), and stated that the red powder formed was insoluble in carbon disulphide. Many years later, Berzelius (*Ann. Phys. Chem.*, 1843, **59**, 77) investigated the formation and properties of red phosphorus, and recognised that it was an allotropic modification of the element. Schrötter (*Denkschr. K. Akad. Wiss. Wien Math. Naturw. Klasse*, 1850, **1**, 1—12) used carbon disulphide for the separation of red phosphorus from yellow phosphorus, claiming that he was the first to effect the separation by this means.
W. P. S.

The Valency of Boron. J. BÖESEKEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **26**, 97—111).—It has been shown by Hermans (this vol., i, 557) that pyrocatecholboric acid, which is a considerably stronger acid than boric acid, must in all probability contain quinquevalent boron. This new type of boron compound

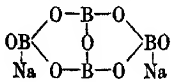
can readily be explained by, and lends considerable support to, the Lewis-Langmuir theory of valency. The quinquevalency of boron in these compounds is explained on the same lines as that of the ammonium compounds, but whereas the nitrogen atom has to lose an electron in order to become quinquevalent, thereby becoming an electropositive ion, the boron atom has to gain an electron, forming an electronegative ion. The oldest known type of compound in which boron is to be regarded as quinquevalent is the type HBF_4. In boron fluoride, BF_3, the outer electron shell of the boron atom contains six electrons, shared in pairs with the fluorine atom. When combining with another molecule of hydrogen fluoride, the boron atom completes its octet by sharing with the new fluorine atom one of the electrons of the latter and a hydrogen electron. By taking the hydrogen electron, however, it forms the negative ion, BF_4', and the positive ion, $H^{\cdot}$. It follows that when boron is functioning as a quinquevalent atom four of its valencies are non-polar and the fifth polar, as in the case of nitrogen.

Boron can also function as a quadrivalent element. This is accomplished when a normal boron compound such as BF_3 combines with a molecule containing two available electrons in the outer shell of one of its atoms, for instance, ammonia. Thus the stable compound, BF_3,NH_3, can be formulated as in the annexed diagram, in which the boron atom appears truly quadrivalent, as does the nitrogen.

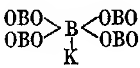


The constitution of the strongly acid compounds formed by boric acid with organic hydroxy-compounds containing favourably situated hydroxyl groups can be explained in a similar way. Some of these are not known as free acids, but only as salts of a metal such as potassium, which readily cedes an electron. Their formation is favoured when the organic residue has an acidic character. Thus in pyrocatecholboric acid the four oxygen atoms of the two pyrocatechol residues are bound to the boron atom each by two electrons. This can only take place when one electron is ceded by a hydrogen or metal atom. The resulting complex acid must therefore be a mono-basic acid.

The unsaturated character of boric acid as a derivative of tervalent boron leads to the formation of stronger poly-boric acids, which must be derivatives of quinquevalent boron. Borax has the formula I and potassium pentaborate, KB_5O_8, probably the formula II.



(I.)



(II.)

II. In nitrogen boride, BN, which is an extraordinarily infusible, stable substance, it may be supposed that continuous polymerisation of the simple BN molecules has taken place, so that each

element is in effect quadrivalent as in the compound NH_3,BF_3 discussed above. The structure of the compound would then be similar to that of carbon in the diamond. The valency here becomes identical with Werner's co-ordination value as expressed, for instance, in the formula $[BF_4]H$. A few other compounds of boron, including the hydrides, are discussed. E. H. R.

Boron Hydrides. VI. The Simplest Boron Hydrides. ALFRED STOCK and ERNST KUSS (*Ber.*, 1923, **56**, [*B*], 789—808).—An extension of previous work (A., 1915, ii, 340, and earlier abstracts). The decomposition of the so-called magnesium boride by acids has been re-examined with the help of much larger quantities of material. The isolation and characterisation of the various boron hydrides are greatly complicated by the presence of silicon hydrides, which cannot be completely avoided, as it has not been found possible to obtain magnesium completely free from silicon, which is largely converted by acids into silicon hydrides whereas, even under the most favourable conditions, boron hydrides are only produced in extremely small amount. On the other hand, the use of the authors' vacuum process and the substitution of fractional condensation for fractional distillation have greatly facilitated the investigations. Tetraborane and diborane have been examined in greater detail. A product to which the composition B_6H_{12} was previously assigned provisionally is shown to be a mixture of B_4H_{10}, B_5H_9, B_6H_{10}, and silicon hydrides.

The decomposition of "magnesium boride" by hydrochloric acid is most advantageously effected by gradually adding it to an excess of the acid at 40—50° (the latter temperature must not be exceeded). The necessary apparatus for the automatic addition is fully figured and described in the original. The gas is washed with water, dried successively with calcium chloride and phosphoric oxide, and condensed in two vessels cooled with liquid air. The separation and purification of the components of the mixture thus obtained are chiefly effected by fractional condensation. Boron hydrides more volatile than tetraborane do not appear to be formed. Diborane is not present in the crude gas; monoborane and triborane could not be detected even in traces.

The following individual hydrides are described. Tetraborane, B_4H_{10}, has m. p. −120·0° (−119·7°), d^{-70} 0·59, d^{-35} 0·56. Its vapour tension has been measured at the following temperatures: −113·2°, 0·2 mm.; −107·9°, 0·4 mm.; −98·0°, 0·8 mm.; −91·1°, 1·0 mm.; −86·3°, 1·9 mm.; −77·8°, 3·2 mm.; −75·1°, 4·0 mm.; −72·3°, 5·0 mm.; −70·2°, 5·9 mm.; −66·0°, 8·5 mm.; −63·2°, 10·8 mm.; −57·4°, 16·7 mm.; −53·3°, 22·2 mm.; −52·2°, 24·2 mm.; −46·7°, 34·4 mm.; −43·8°, 41·4 mm.; −39·2°, 55 mm.; −36·8°, 64 mm.; −33·7°, 76 mm.; −28·7°, 101 mm.; −27·5°, 108·5 mm.; −21·4°, 150 mm.; −16·1°, 188 mm.; −10·6°, 247 mm.; −6·5°, 295 mm.; −2·0°, 369 mm.; 0°, 388 mm.; +4·9°, 469 mm.; +10·0°, 572 mm.; +15·1°, 697 mm.; +17·6°, 755 mm. Even when highly purified, tetraborane decomposes fairly rapidly at the atmospheric temperature into hydrogen, diborane, and a number

of less volatile hydrides. The hydrogen which is thus liberated is an extremely powerful reducing agent which converts disilane and the higher hydrides of silicon into monosilane. Tetraborane and ethane yield hydrogen, diborane, the hydride B_5H_9, and a pale yellow, crystalline substance containing boron, carbon, and hydrogen.

The analysis of tetraborane and the other hydrides is effected by thermal decomposition into boron and hydrogen. The volume of the latter is measured. The boron is estimated by direct weighing and also titrimetrically after oxidation to boric acid. The necessary apparatus is figured and described.

Diborane, B_2H_6, obtained by heating tetraborane in a sealed tube, is very stable in the absence of moisture and grease. It has m. p. −165·5°, tensions, 6·0 mm./−148·3°, 11·3 mm./−144·8°, 20·3 mm./−139·0°, 30·7 mm./−134·9°, 48 mm./−130·5°, 52 mm./−129·5°, 83 mm./−124·5°, 122 mm./−119·9°, 187 mm./−115·2°, 272 mm./−109·2°, 361 mm./−104·5°, 521 mm./−99·3°, 608 mm./−96·4°, 637 mm./−95·5°, 701 mm./−93·8°, 748 mm./−92·75°, d^{-112} 0·44. Diborane does not appear to undergo dissociation at any temperature between −24° and +155°. Diborane reacts with hydrogen bromide in the presence of aluminium bromide at 80—90° to give hydrogen and monobromodiborane; the latter is, however, very unstable and becomes converted largely into boron tribromide and diborane: $6B_2H_5Br=2BBr_3+5B_2H_6$.

The *hydride*, B_5H_9, is present in small quantity in the higher boiling fractions of the "crude condensate," but its isolation from this source is extremely difficult and it is more readily obtained in the homogeneous condition from the products of the decomposition of tetraborane at 100°. It is a colourless, mobile, not highly refractive liquid with an extremely unpleasant odour; it is the noxious component of the crude boron hydrides. It is slowly decomposed by water, but otherwise fairly stable. It has m. p. −46·9°, tensions, 4·8 mm./−41·3°, 7·4 mm./−35·6°, 12 mm./−28·9°, 15·1 mm./−25·1°, 21·1 mm./−20·0°, 28·5 mm./−14·9°, 37·8 mm./−9·9°, 49·0 mm./−5·0°, 65 mm./0°, 84 mm./+6·0°, 111 mm./+11·2°, 131 mm./+15·1°, d^0 0·61. It is slowly hydrolysed by water at 90° into hydrogen and boric acid: $B_5H_9+15H_2O=5H_3BO_3+12H_2$.

The *hydride*, B_6H_{10}, is isolated from the crude condensate. It is a colourless, moderately highly refractive liquid which is less mobile and not so unpleasant in odour as the other boron hydrides. It has m. p. −65·1°, tension 7·2 mm./0°, d^0 0·70. It is slowly hydrolysed by water at 90° into boric acid and hydrogen. It slowly decomposes when preserved in daylight at the atmospheric temperature, giving small quantities of hydrogen and diborane and mainly a yellow, crystalline solid of the possible composition $B_{26}H_{36}$.

The thermal decomposition of diborane at 300° gives mainly boron and hydrogen. At lower temperatures (100—200°) and higher pressures, other products, chiefly $B_{10}H_{14}$, and further solid hydrides, are also formed. Tetraborane is converted at 100° into diborane,

B_5H_9, and other substances; at 300°, it yields mainly boron and hydrogen. The hydride, B_5H_9, is much more stable than tetraborane at 300°, and is only partly decomposed into boron and hydrogen. Under similar conditions the hydride, B_6H_{10}, also suffers decomposition less readily than tetraborane.

Diborane does not resemble disilane in its action towards sodium amalgam, which causes condensations which have not been investigated completely. Similar reactions appear to take place with tetraborane.

Diborane and tetraborane react readily with ammonia to form liquid and solid products. They do not appear to have any action on acetylene when cold, but if the mixtures are heated at 100° or rapidly compressed an explosive change occurs accompanied by the separation of a solid, brown substance. If the mixtures are warmed gently, aromatic condensation products are formed which evolve hydrogen when treated with water. H. W.

The Melting and Working Properties of Boric Oxide Glasses with Special Reference to the Sodium Borosilicates. VIOLET DIMBLEBY, F. W. HODKIN, M. PARKIN, and W. E. S. TURNER (*J. Soc. Glass Tech.*, 1923, 7, 57—72).—Three series of sodium borosilicate glasses were prepared containing, respectively, 20, 10, and 5% of sodium oxide. In the first series, the amount of boric oxide was varied between 0 and 45%, in the second between 15 and 50%, and in the third between 20 and 45%. In every case, homogeneous glasses were obtained with no evidence of segregation. High proportions of boric oxide give unstable glasses. Those with more than 40% B_2O_3 in the first and second series or more than 35% B_2O_3 in the third series quickly developed a white film, the most readily disintegrated being those containing the smallest proportion of sodium oxide. Melting and refining proceed more rapidly with increasing proportion of boric oxide, but the fluxing action of borax or boric oxide is not so great as that of sodium carbonate. The rate of change of viscosity with temperature increases rapidly with increasing boric oxide concentration. The glasses of the first and second series showed no devitrification when worked. E. H. R.

The Influence of Boric Oxide on the Annealing Temperature of Borosilicate Glasses. S. ENGLISH and W. E. S. TURNER (*J. Soc. Glass Tech.*, 1923, 7, 73—76).—In the case of sodium borosilicate glasses containing 20% of sodium oxide, as the proportion of boric oxide increases from 0 to 46% the annealing temperature rises steadily from 505° to a maximum of 570° at about 16—17% B_2O_3, and then falls gradually to about 521°. In the case of glasses containing 10% of sodium oxide, the annealing temperature falls steadily from 597° with 12·45% B_2O_3 to 495° with 46·07% B_2O_3. It is probable, however, that had glasses in this series been obtainable with 0–12% B_2O_3, a maximum annealing temperature would have been found in the neighbourhood of 12% B_2O_3. E. H. R.

Active Charcoal. I. Nature of the Activity. OTTO RUFF [with SUSANNE MUGDAN, ERNST HOHLFELD, and FRITZ FEIGE] (*Kolloid Z.*, 1923, **32**, 225—232).—The authors describe a number of experiments designed to ascertain the cause of the activity of certain varieties of charcoal in the adsorption of gases and liquids. Charcoal prepared from ashless filter-paper, coconut, and wood were investigated with respect of their activity in connexion with the temperature of formation, ash content, and the nature of the ash. As the result of the experiments, it is shown that the activity of charcoal is due to the atoms and atom groups of foreign materials bound to the surface of the charcoal. These atoms are the cause of the specific properties of active charcoal, and they are characterised by the firmness of their linking to the carbon atoms on the surface. Other atoms can also attach themselves to the surface, but these are easily replaced by others and are not firmly bound. With every change in the nature of the surface of the charcoal the adsorptive properties are markedly changed. J. F. S.

The Molecular Complexity of Graphite at High Temperatures. A. JOUNIAUX (*Bull. Soc. chim.*, 1923, [iv], **33**, 260—267).—It has already been shown by numerous investigators that the higher the temperature at which carbon is liberated by the decomposition of its compounds, the greater the percentage of graphite which it contains, until, at about 3500°, the temperature of sublimation of carbon, the product consists of pure graphite, and, further, all varieties of amorphous carbon are converted into graphite at the temperature of the electric arc. The system amorphous carbon–graphite therefore behaves as an univariant system, with a position of equilibrium corresponding with each temperature. On cooling the system, a false equilibrium may be attained, and the physical constants determined at low temperatures will be those of mixtures in proportions varying according to the temperature at which the carbon was prepared, but at high temperatures (above 3000°) the constants are those of graphite, and the specific heat, for example, is in accord with Dulong and Petit's law. The above considerations justify the result obtained in the determination of the molecular weight of graphite from cryoscopic observations on solutions of carbon in iron and cobalt, M, the molecular weight, being given by the formula $0{\cdot}02T/L(c/p_1-p_2)_0$, where T is the absolute temperature and L the latent heat of fusion of the solvent. At the temperatures in question, about 1500°, M was 15·4 in the one case and 15·1 in the other, values in fair agreement with that obtained from the specific heat of graphite at that temperature and Dulong and Petit's law, namely, 14·5. The graphite molecule at these and higher temperatures would therefore appear to be monatomic at least when in solution in the metal. G. F. M.

Preparation of Thiocarbonyl Chloride. REMO DE FAZI (*Gazzetta*, 1923, **53**, i, 175—176).—Although the action of iron on thiocarbonyl tetrachloride may result in the formation of ferrous chloride and carbon tetrachloride (cf. Frankland, Garner, Challenger, and Webster, A., 1920, ii, 753), under special conditions it proceeds

in accordance with the equation $CCl_3 \cdot SCl + Fe = FeCl_2 + CSCl_2$; when certain catalysts are used, a yield of 80% of thiocarbonyl chloride is obtainable. T. H. P.

Revision of the Atomic Weight of Silicon. The Analysis of Silicon Tetrachloride and Tetrabromide. G. P. BAXTER, P. F. WEATHERILL, and E. W. SCRIPTURE, jun. (*Proc. Amer. Acad. Arts Sci.*, 1923, 58, 245—268; cf. A., 1920, ii, 487).—Consistent results, agreeing to about one part in two thousand, yield a value of 28·063. CHEMICAL ABSTRACTS.

Silicon Hydrides. XIV. Trichloro- and Tetrachloro-monosilanes, $SiHCl_3$ and $SiCl_4$. ALFRED STOCK and FRIEDRICH ZEIDLER (*Ber.*, 1923, 56, [*B*], 986—997).—Trichloromonosilane has been prepared from technical copper silicide and hydrogen chloride at 300° and purified by fractional distillation and condensation in the authors' vacuum apparatus. The isolation of the pure compound is very tedious, since the main impurities, hydrogen chloride and silicon tetrachloride, are very obstinately retained and the former appears to be continuously produced probably owing to the slight but unavoidable water content of the glass. The pure material has m. p. −126·6° or −126·4°, d^0 1·35, tensions 0·7 mm./−85·0°, 1·3 mm./−80·1°, 1·9 mm./−75·0°, 2·8 mm./−70·1°, 4·1 mm./−65·2°, 6·0 mm./−60·5°, 9·4 mm./−54·2°, 13·0 mm./−50·0°, 19·0 mm./−44·9°, 25·3 mm./−40·2°, 34·9 mm./−35·5°, 45·5 mm./−30·5°, 60·5 mm./−25·3°, 80 mm./−20·3°, 104 mm./−15·2°, 132 mm./−10·5°, 167 mm./−5·9°, 218 mm./0°, 275 mm./+5·4°, 338 mm./10·5°, 412 mm./15·3°, 501 mm./20·2°, 598 mm./25·0°, 717 mm./30·1°, 765 mm./32·0°, b. p. 31·8°/760 mm. Trichloromonosilane is remarkably stable towards heat, but at 900° suffers almost quantitative decomposition into silicon, hydrogen, hydrogen chloride, silicon tetrachloride, and a trace of liquid less volatile than the latter. It is not affected by aluminium chloride at 175°. It reacts readily with sodium amalgam, obviously in accordance with the scheme $SiHCl_3 + 3Na \longrightarrow 3NaCl + (SiH)_x$, since volatile compounds are not produced in appreciable amount. It reacts with ammonia in the gaseous phase under diminished pressure, and at the atmospheric temperature in accordance with the equation $2SiHCl_3 + 9NH_3 = [SiH(NH)]_2NH + 6NH_4Cl$. The same products are obtained when the components are successively condensed in the same vessel by means of liquid air, and the mixture is slowly warmed. If the product is gradually heated, the imide becomes decomposed, mainly in accordance with the scheme $[NH{:}SiH]_2NH \longrightarrow 2SiHN + NH_3$, and at about 250° the ammonium chloride commences to sublime. A quantitative separation of the two compounds cannot, however, be effected in this manner. The action of hydrogen chloride on the compound $[NH{:}SiH]_2NH$, proceeds mainly according to the scheme $[NH{:}SiH]_2NH + 9HCl = 2SiHCl_3 + 3NH_4Cl$, but is accompanied by difficultly explicable side changes.

Even at low temperatures, silicon tetrachloride does not appear to react with more than seven molecular proportions of ammonia

in accordance with the equation $SiCl_4+7NH_3=Si(NH_2)_2{:}NH+4NH_4Cl$. The amide-imide is quantitatively converted when warmed to 0° or the atmospheric temperature into the di-imide, $Si(NH)_2$. When the mixture of the latter with ammonium chloride is treated with hydrogen chloride, it is transformed into silicon tetrachloride and ammonium chloride, $Si(NH)_2+6HCl=SiCl_4+2NH_4Cl$.

Trichloromonosilane is immediately decomposed by an excess of water into solid, non-volatile, polymerised dioxodisiloxane, $[SiH(O)]_2O$ (silicoformic anhydride), which has been isolated in the homogeneous condition and is then remarkably stable towards water. In the gaseous condition, the chloro-compound only reacts slowly with a deficiency of water vapour, without giving any indication of the formation of products intermediate between it and dioxodisiloxane. Attempts to isolate the latter in a less highly polymerised form by decomposing trichloromonosilane in the presence of benzene were unsuccessful. It gives indications of its ability to form salts in the absence of water.

The halogenated monosilanes appear to react uniformly with water and ammonia. Monochlorosilane yields the substances $(SiH_3)_2O$ and $(SiH_3)_3N$, which are unimolecular and volatile. The dichloro-compound gives the products SiH_2O and $SiH_2{:}NH$, which can be preserved for a short time in the volatile form with low molecular weight, but rapidly become associated to non-volatile polymerides. The trichloro-derivative gives the derivatives $[SiOH]_2O$ and $[NH{:}SiH]_2NH$, which do not occur in volatile modifications of low molecular weight, whereas silicon tetrachloride yields $Si(OH)_2O$ and $Si(NH_2)_2{:}NH$, which are only known in the associated condition; the latter substances readily lose water and ammonia, respectively, and pass into silicon dioxide and di-imide.

H. W.

Positive-ray Analysis of Potassium, Calcium, and Zinc. A. J. Dempster (*Physical Rev.*, 1922, 20, 631—638; cf. A., 1921, ii, 402; 1922, ii, 417).—The charge deflected by a constant magnetic field through a fixed slit into a Faraday cylinder is measured as a function of the voltage accelerating the rays, and curves showing maxima corresponding with the various isotopes are plotted. Aston's results for potassium (39, 41) were confirmed; calcium has isotopes at 40 and 44, and zinc at 64, 66, 68, and 70. In the cases of potassium and calcium, the ratios of the intensities give average atomic weights in good agreement with the accepted values. When accurate and trustworthy results for the relative proportions of all the isotopes of an element are available, comparison of the calculated and observed atomic weights will give a measure of the packing effect, or divergence of the atomic weights of the isotopes from integral values.

A. A. E.

Precision Measurements of Crystals of the Alkali Halides. Wheeler P. Davey (*Physical Rev.*, 1923, [ii], **21**, 143—161).—By the use of Hull's powder method, the *X*-ray diffraction patterns of the alkali halides have been compared with that of sodium

chloride. The following measurements of the side of the unit cube in each case, that of sodium chloride being assumed to be 2·814 Å., are given; the figures within brackets represent the crystal densities, computed from the X-ray data, assuming that of sodium chloride to be 2·163. Lithium fluoride, 2·007±0·004 Å. (2·646±0·016); chloride, 2·566±0·003 (2·069±0·006); bromide, 2·745±0·003 (3·463±0·010); iodide, 3·537±0·005 (2·494±0·015). Sodium fluoride, 2·310±0·002 (2·809±0·008); bromide, 2·968±0·003 (3·246±0·010); iodide, 3·231±0·003 (3·665±0·011). Potassium fluoride, 2·664±0·003 (2·534±0·008); chloride, 3·138±0·003 (1·990±0·006); bromide, 3·285±0·003 (2·768±0·008); iodide, 3·525±0·004 (3·125±0·009). Rubidium fluoride, 3·663±0·004 (3·504±0·010); chloride, 3·267±0·003 (2·859±0·009); bromide, 3·418±0·003 (3·415±0·010); iodide, 3·655±0·004 (3·557±0·011). Cæsium fluoride, 3·004±0·003 (4·617±0·014); chloride, 4·118±0·004 (3·973±0·012); bromide, 4·287±0·004 (4·453±0·013); iodide, 4·558±0·005 (4·523±0·014). There is general, although not complete, agreement with densities determined by other methods.

A. A. E.

The Structure of Halogen Salts Based on their Compressibility. IDA WOODWARD (*Phil. Mag.*, 1923, [vi], **45**, 882—895).—A theoretical paper in which calculations, based on Thomson's hypothesis (cf. A., 1922, ii, 252, 355), are made of the compressibilities of the cubic crystals, the chlorides, bromides, and iodides of sodium and potassium, and the chloride and bromide of silver. The following values were obtained: NaCl, 4·139; NaBr, 5·099; NaI, 6·990; KCl, 5·061; KBr, 6·351; KI, 8·660; AgCl, 2·30; AgBr, $2·68\times10^{-12}$. These are in good agreement with the experimental values of Richard and Jones. In addition, the specific photoelectric effect and the specific inductive capacity for the sodium and potassium salts have been calculated from the atomic diameters given by W. L. Bragg (cf. A., 1920, ii, 537). The calculated values of K, as far as there are experimental data, are seen to lie between the extreme observed values. W. E. G.

The Solubility of Potassium Carbonate in Water. P. P. RUBCOV (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 220—224).—The discrepancies between solubility curves for potassium carbonate, as obtained by Ozanne, by Poggiale (1843), by Gerlach (1862), and by Mulder (*Scheikund. Verhandel*, 1864, 96) are pointed out, and the solubility of potassium carbonate in water at 16·5° and at 19·5° found to agree with the corresponding values obtained by Mulder. R. T.

The Crystalline Structure of Sodium Bromate and Sodium Chlorate. N. H. KOLKMEIJER, J. M. BIJVOET, and A. KARSSEN (*Z. Physik*, 1923, **14**, 291—295).—The relative intensities of the lines in the X-ray spectrum of sodium bromate, obtained by reflection in various planes of the crystal, as determined and calculated by the authors (A., 1921, ii, 200) and by Vegard (this vol., ii, 162) are compared, and it is concluded that the authors' values of the

parameters of the crystal are the more accurate. It is pointed out that the crystalline structure of sodium bromate and sodium chlorate, as determined by Dickenson and Goodhue (A., 1922, ii, 145), agrees with the structure found by the authors and by Vegard, and that the values of the crystalline parameters deduced therefrom are in close agreement with the values obtained by the present authors. J. S. G. T.

Fluorophosphate and Fluorovanadate of Sodium Extracted from Bauxite. TRAVERS (*Bull. Soc. chim.*, 1923, [iv], **33**, 297—306).—The octahedral crystals deposited on cooling a sodium hydroxide extract of bauxite after separation of the aluminium are composed of an isomorphous mixture in varying proportions of a double fluoride and phosphate, and a double fluoride and vanadate of sodium, having the composition $2Na_3PO_4,NaF,19H_2O$ and $2Na_3VO_4,NaF,19H_2O$, respectively. The crystals are usually mixed with traces of prismatic crystals of $Na_2CO_3,10H_2O$. Using a 2·5% solution of sodium hydroxide free from carbonate for the extraction, the crystals contained 76% of the fluorophosphate, 22·2% of the fluorovanadate, and 1·5% of carbonate. The proportion of the fluorovanadate increases somewhat as the concentration of the hydroxide is increased, and diminishes owing to hydrolysis if weaker hydroxide solution or water is employed in the preparation. The fluorophosphates and fluorovanadate are not complex salts, but double salts which are dissociated in solution into their constituents, at least in the neighbourhood of 100°, as on seeding a hot saturated solution with sodium phosphate or vanadate prisms are first formed, which are progressively transformed into octahedra of the double salt as the solution cools.
G. F. M.

The Acid Borates of Sodium. I. F. PONOMAREV (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 229—240).—The difficulty of obtaining the higher borates in a crystalline form is overcome by heating strongly one end of a long platinum boat containing mixtures of borax and boric oxide, so that, in some part of the mass, cooling conditions must be favourable for the formation of crystalline nuclei. In this way, the fusion diagram for the system borax-boric oxide is constructed, and the melting points of the compounds formed are determined. The fusion diagram indicates the formation of two hitherto unknown compounds, with a composition corresponding with $Na_2O,3B_2O_3$, m. p. 694°, and $Na_2O,4B_2O_3$, m. p. 783°, capable of forming mixed crystals with each other, and with boric oxide. Pure crystalline boric oxide was not obtained, although crystals containing only 3% of sodium oxide separated from the 90% boric oxide mixture. R. T.

Constitution of Per-salts, more especially of Percarbonates and Perborates. M. LE BLANC and R. ZELLMANN (*Z. Elektrochem.*, 1923, **29**, 179—187, 192—198).—The literature of the preparation of percarbonates and perborates is briefly reviewed and

an investigation of the conditions determining the electrolytic preparation of sodium percarbonate by the electrolysis of solutions of sodium carbonate detailed. A platinum wire anode and a nickel wire cathode were employed. Experiments were made at 0° and 15°. The results indicate that the percentage yield, calculated from the current employed, fell off with time and was less for an anode- or cathode-current density of 32 amperes per sq. dcm. than for 22 amperes per sq. dcm. A maximum initial percentage efficiency equal to 74% was obtained by the electrolysis at 0° of a solution containing 60 g. of sodium carbonate per litre, employing a current density of 22 amperes per sq. dcm. of anode or cathode surface. The percentage efficiency of the process fell to 40% after two hours' electrolysis. The efficiency is initially reduced owing to the presence of sodium hydrogen carbonate, and during the electrolysis carbon dioxide is displaced from the latter by hydrogen peroxide. The increased efficiency of production of sodium perborate by the electrolysis of a solution of borax, due to the addition of sodium hydrogen carbonate to the electrolyte, as observed by Arndt and Hantge (A., 1922, ii, 569), is attributable mainly to the decreased solubility of the perborate in the resulting solution. By a modification of the process due to Wolffenstein and Peltner (A., 1908, ii, 180), the per-salts $Na_2C_2O_6$ and $NaHCO_4$ were prepared of a greater purity than those obtained by the latter. The salt, $Na_2C_2O_6$, is hydrolysed in the same manner as persulphates and perphosphates, with production of $NaHCO_4$. It is shown that all methods of preparation of sodium perborate are based on the reaction $NaBO_2+H_2O_2=Na[BO_2,H_2O_2]$. This last compound is termed a ψ-perborate. Sodium perborate may be prepared in accordance with the equation $NaOOH+H_3BO_3=NaBO_3+2H_2O$. Potassium ψ-perborate is prepared by adding 3% hydrogen peroxide solution to a dilute solution of potassium metaborate. The constitution and classification of per-salts are discussed. Amongst percarbonates, $NaHCO_4$ and $Na_2C_2O_6$ are true percarbonates. The composition of the compound $Na_2CO_4,1\frac{1}{2}H_2O$, corresponds really with the formula

$$Na_2CO_3,\tfrac{1}{2}H_2O_2,\tfrac{1}{2}H_2O,$$

whilst the compound Na_2CO_5 prepared by Wolffenstein and Peltner is really a mixture of NaOOH and $NaHCO_4$. Potassium perborate, $2KBO_3,H_2O$, prepared by von Girsewald and Wolokitinn (A., 1909, ii, 312) is a true per-salt. J. S. G. T.

The Acid Reaction of Ammonium Salts to Litmus. Cam. Gillet (*Bull. Soc. chim. Belg.*, 1923, **32**, 178—179).—The observation of Reichard (A., 1904, ii, 30) that blue litmus paper, when moistened by the solution of an ammonium salt and allowed to dry in air, turns red is confirmed. His explanation of oxidation fails, as the same phenomenon occurs in an atmosphere of hydrogen. The author shows that the reddening is due to dissociation of the ammonium salt with subsequent volatilisation of ammonia in presence of the blue potassium salt derived from litmus with which the paper is coloured. H. J. E.

The Sulphides of Ammonium. John Smeath Thomas and Richard William Riding (T., 1923, **123**, 1181—1189).

Calcium Iodide. Tomozô Mizutani (Japan. Pat. 40944).—Calcium iodide is prepared from calcium chloride and an alkali iodide by mixing their saturated alcoholic solutions in the ratio of 1 : 2 mols. The whole process should be carried out in the absence of air. The sodium or potassium chloride first precipitated is filtered off, and the mother-liquor is concentrated in a vacuum and placed in the dark. About 10 g. of calcium iodide are produced from 20 g. of hydrated calcium chloride. K. K.

The Dehydration of Gypsum. Pierre Jolibois and Pierre Lefebvre (*Compt. rend.*, 1923, **176**, 1317—1320; cf. van't Hoff, Armstrong, Hinrichsen, Weigert, and Just, A., 1904, ii, 35).—Dehydration of hydrated calcium sulphate in dry air gives no indication of the formation of $2CaSO_4,H_2O$ as an intermediate substance, but the loss of weight measured on heating gypsum in a closed vessel at temperatures ranging up to 160° shows the existence of a limit of dehydration corresponding with the hemihydrate. Above 160°, further loss of water occurs, whilst at 200° it is complete and rapid. H. J. E.

Electrometric Study of the Neutralisation of Phosphoric Acid by Calcium Hydroxide. Gerald L. Wendt and Alfred H. Clarke (*J. Amer. Chem. Soc.*, 1923, **45**, 881—887).—The electrometric titration of phosphoric acid with solutions of calcium hydroxide and the titration of calcium hydroxide with phosphoric acid have been investigated, using the apparatus described by Hildebrand for electrometric titrations (A., 1913, ii, 721). Graphic representation of both the slow and the rapid electro-titration of phosphoric acid with calcium hydroxide shows that the existence of dicalcium phosphate is transitory, so that under equilibrium conditions only the mono- and tri-calcium salts are present. The rearrangements involved in these changes are partly responsible for the difficulty in titrating monocalcium phosphate for its "neutralising value." J. F. S.

The Reflection of Röntgen Rays from certain Remarkable Reticular Planes in Calcite. Ch. Mauguin (*Compt. rend.*, 1923, **176**, 1331—1334; cf. W. L. Bragg, A., 1914, ii, 181).—A critical discussion of the interpretation of the experimental results bearing on the spatial arrangement of atoms in calcite. The conclusions afford a new confirmation of Bragg's hypothesis.
H. J. E.

Studies on the Dolomite System. I. The Nature of Dolomite. Allan Ernest Mitchell (T., 1923, **123**, 1055—1069).

Diagrams of the Solidification of the System $MgCl_2$-KCl-$BaCl_2$. C. Matignon and J. Valentin (*Bull. Soc. chim.*, 1923, [iv], **33**, 267—280).—The principal points of the diagrams of the binary systems $MgCl_2$-KCl and $MgCl_2$-$BaCl_2$ obtained by previous

workers were re-verified, and the same results obtained except for the second eutectic of the former system, which was found to be at 440° instead of 425° as given by Menge (A., 1911, ii, 982). The solidification of the ternary system was studied by means of a Le Chatelier platinum-rhodium thermoelectric couple in conjunction with a Rengade recording camera (*Bull. Soc. chim.*, 1909, [iv], 7, 934), the boiling point of sulphur and the melting point of sodium chloride being employed as points of reference on the temperature scale. The materials were melted in a platinum crucible, and the results obtained are recorded by means of triangular diagrams and tables. G. F. M.

Solubility between Cadmium and Thallium in the Solid State. CLARA DI CAPUA (*Atti R. Accad. Lincei*, 1923, [v], 32, i, 282—285; cf. Kurnakov and Pushin, A., 1902, ii, 139; Bornemann, *Metallurgie*, 1910, 7, 103).—The author has investigated the diagram of state of cadmium–thallium alloys by Plato's method (A., 1906, ii, 521; 1907, ii, 239). The eutectic corresponds with about 1·82% of thallium, and the initial solidification curve closely resembles that given by Kurnakov and Pushin, but different results are obtained in so far as the extension of the eutectic horizontal is concerned. On the cadmium side, the annulment of the eutectic arrest corresponds virtually with the pure metal, whilst on the thallium side the eutectic arrest is annulled at a concentration of about 2·5% of cadmium; thus appreciable solubility of thallium in cadmium is excluded, whereas cadmium is slightly soluble in thallium in the solid state. The results of conductivity and cryoscopic measurements are in agreement with these conclusions. T. H. P.

Electrical Conductivity and the Chemical Constitution of Alloys. I. The System Lead–Thallium. W. GUERTLER and A. SCHULZE (*Z. physikal. Chem.*, 1923, **104**, 269—300).—The use of electrical conductivity measurements for determining the constitution of alloys is discussed, and it is shown to supplement the method of thermal analysis, in the following points. The determination of the commencement of a crystallisation can generally be ascertained by the thermal method, but only in rare cases by the conductivity method. The determination of the end of a crystallisation (that is, the extent of the eutectic horizontal between two saturated mixed crystals), and the determination of the exact position of the curve of the mixed crystals which are in equilibrium with the liquid phase during melting, cannot be found exactly by thermal analysis, but are obtained very sharply from conductivity measurements. The fixing of the saturation boundaries of non-continuous mixed crystal series is achieved very exactly by the conductivity method, but not by the thermal method. In the absence of mixed crystals, the existence of a compound may be overlooked by the conductivity method, because of the ill-defined inflection of the conductivity–concentration curve, but this is not likely by thermal analysis or when the temperature–resistance curve is used. In series of mixed crystals, thermal analysis does not give a clear indication when maxima or minima appear in the curves,

but conductivity measurements indicate the existence of a compound. The testing of a system with respect of its stability is often not possible by the thermal method, but this can be tested very sharply by the conductivity method. Transitions and chemical actions, on account of the small thermal effect, often remain unrecognised by the thermal method, but are definitely indicated by resistance measurements. The electrical conductivity of lead–thallium alloys has been determined over the temperature range 0—260° for the whole range of compositions by the method previously described and used for gold–iron alloys (this vol., ii, 284). Resistance–temperature curves have also been constructed which are shown to be continuous over the range 100—22·5% of lead; a small discontinuity is found between 20% and 6·5% of lead at temperatures between 130° and 150°. The curves for alloys containing less than 6% of lead show a definite discontinuity, which indicates a transition. Diagrams are shown indicating the regions in which mixed crystals of α-thallium with lead, β-thallium with lead, and lead with a form of thallium which is unknown in the free state, exist. There is no evidence of the existence of a compound $PbTl_2$, since the resistance curves of the alloys with 25, 30, 33, and 40% of lead run parallel to one another. The results in general are in keeping with those deduced by other authors from thermal data. The transition of the mixed crystal series rich in thallium has been followed completely, and the diagram obtained previously from thermal data has thereby been completed. Since the conductivity curve and that of the temperature coefficient for the concentrations 30—40% of thallium are perfectly continuous, Kurnakov's contention (A., 1902, ii, 139) that a maximum on the melting point–composition curve does not indicate a chemical compound, is justified. J. F. S.

Crystallographic Transformations in Lead–Bismuth–Tin Alloys. Karl Bux (*Z. Physik*, 1923, **14**, 316—327).—Crystallographic transformations similar to those first observed by Hauser (*ibid.*, 1921, **5**, 220) in the case of the ternary lead–bismuth–tin eutectic are shown to occur at various temperatures in the case of all other ternary alloys of the system, the only apparent exception being the alloy Pb_3BiSn_4. The phenomenon has been investigated by examining microscopically the surface of cooling crystals of the various alloys at various temperatures. Amongst binary alloys of the series, the phenomenon occurs probably only in the case of the lead–bismuth alloys, but thermal investigations are necessary to decide this point definitely. The transformation temperature depends on the composition of the alloy, the dependence on the proportion of lead present being very pronounced. A variation in the proportion of tin affects the transformation temperature only very slightly. The following transformation temperatures were determined: $PbBi_4Sn_4$, 71°; $Pb_2Bi_4Sn_4$, 54°; $Pb_3Bi_4Sn_4$, 46°; $Pb_5Bi_4Sn_4$, $Pb_7Bi_4Sn_4$, and $Pb_9Bi_4Sn_4$, about 40°; $Pb_3Bi_4Sn_1$, 40°; $Pb_2Bi_4Sn_7$, 41°; $Pb_3Bi_4Sn_9$, 45°; Pb_3Bi_4, 70°. The phenomena observed can be explained by assuming that the temperature of transformation of one allotropic modification of bismuth into the

other is reduced by the addition of lead and tin, the reduction being determined principally by the percentage of lead added. Approximately, eutectic mixtures may be cooled to the respective transformation temperatures without appreciable surface changes occurring. In the case of alloys containing one component largely in excess of that contained in the eutectic, crystallisation occurs before the alloy cools to the transformation temperature. Chilling the alloys causes the transformation phenomenon to be suppressed very considerably. J. S. G. T.

Action of Alkali Hydroxides on Lead Salts. Akira Ogata and Takanori Kai'un (*J. Pharm. Soc. Japan*, 1923, 78—81).—It is generally assumed that lead hydroxide is precipitated on adding an alkali hydroxide to lead nitrate solution. The authors have studied the action of *N*-sodium hydroxide solution on lead nitrate quantitatively and analysed the products of the reaction, the result being summarised as follows: (1) When an insufficient quantity of sodium hydroxide is used the basic nitrate, $Pb(NO_3)\cdot OH$, is precipitated. (2) By using a slight excess of the alkali, a second basic salt, $NO_3\cdot Pb\cdot O\cdot Pb\cdot O\cdot Pb\cdot OH$, is precipitated. As the solubility of $NO_3\cdot Pb\cdot OH$ is small, a comparatively long time is needed for the completion of the above reaction. (3) By adding a large excess of the alkali to the nitrate solution, lead hydroxide is never produced, more basic salts which still contain NO_3-groups being formed. For the preparation of lead hydroxide, lead acetate must be used instead of the nitrate, but the product is $2PbO,H_2O$, not $Pb(OH)_2$ (cf. Schaffner, *Annalen*, 1844, **51**, 175). K. K.

Thallous Hydroxide. R. de Forcrand (*Compt. rend.*, 1923, **176**, 873—876).—Thallous hydroxide is readily obtained in good yield as a yellow, microcrystalline powder by adding to thallous ethoxide in the cold an equal volume of water, and drying the precipitate on porous plates out of contact with air. A determination of the heat of hydration of thallous oxide by finding the difference in the heat of solution of the oxide and hydroxide in dilute hydrofluoric acid gave a value 3·117 Cal., compared with 3·231 Cal. found by Thomsen. The heat of hydration is therefore very far removed from that of the oxides of the alkali metals, but thallous hydroxide is nevertheless an equally powerful base, and towards feeble acids, phenols, etc., shows even stronger basic properties than the alkali hydroxides. It can be estimated acidimetrically using phenolphthalein as indicator. G. F. M.

Thallium Compounds. II. The Reduction of Thallic Compounds with Ferrous Sulphate and with Sodium Arsenite. Arthur John Berry (T., 1923, **123**, 1109—1114).

A Prehistoric Greek Axe; Its Composition by Spectral and Chemical Analysis. The Partial Reconstruction of its Metallurgy by Microscopic Metallography. H. Weiss, Dandurand and Dureuil (*Bull. Soc. chim.*, 1923, [iv], **33**, 439—447).—The axe contained 96·4% of copper and 1·25% of arsenic, together with the following elements in much smaller amount: tin 0·1%,

lead 0·12%, iron 0·1%, sulphur 0·25%, oxygen (by difference) 1·78%, and traces of antimony, silver, nickel and cobalt, and zinc. Spectral analysis also showed the presence of distinct traces of chlorine, the presence of which is ascribed to the formation of an oxychloride of copper by the action of salt water on the metal in sunlight. Details are given of the analytical procedure adopted. A photomicrographic study of the metallography of the axe clearly indicated that it was not made from native copper, and that it was cast in a mould and cooled, but not so rapidly as would have occurred had cold water been used as cooling agent. The cast axe had then been subjected to hammering. The origin of the axe is uncertain, but arsenical copper ores are known to have been exploited in the earliest times in Serbia, Armenia, the Caucasus, and in the Sinai district. G. F. M.

The Action of Thiosulphates on Cupric Salts. Henry Bassett and Reginald Graham Durrant (T., 1923, **123**, 1279—1291).

The Interaction of Ammonium Hydroxide with Mercurous Bromide. J. G. F. Druce (*Chem. News*, 1923, **126**, 225—226).—The black precipitate which is produced in this reaction is shown to be a mixture of $NH_2\cdot HgBr$ and metallic mercury. W. E. G.

Chlorites of Mercury and Other Metals. G. R. Levi (*Atti R. Accad. Lincei*, 1923, [v], **32**, 165—169; *Gazzetta*, 1923, **53**, i, 245—249; cf. A., 1922, ii, 567).—*Mercuric chlorite*, $Hg(ClO_2)_2$ (cf. Bruni and Levi, A., 1916, ii, 27), forms a red, crystalline precipitate and, if kept dry in more than very small amount, undergoes rapid decomposition and sometimes spontaneous ignition, with formation of mercuric chloride; it explodes slightly on percussion. *Mercurous chlorite*, $HgClO_2$, a canary-yellow precipitate, was not obtained quite free from mercurous oxide. *Basic mercurous chlorite*, $2HgClO_2,Hg_2O,5H_2O$, forms a cream-yellow precipitate and, like the preceding compound, is readily decomposed when heated or struck. *Mercuriammonium chlorite*, $NH_2(HgOHg)ClO_2$, is highly unstable and explosive and was not obtained pure. *Nickel chlorite* ($+2H_2O$) is not readily exploded on percussion but even in solution decomposes rapidly when gently heated. *Erbium chlorite*, $Er(ClO_2)_3,4H_2O$, obtained as a pink precipitate, decomposes only very slowly when its aqueous solution is boiled. T. H. P.

The Ceric Hydroxide Sol. H. R. Kruyt and (Miss) J. E. M. van der Made (*Rec. trav. chim.*, 1923, **42**, 277—300).—Three ceric oxide sols, differing considerably from each other in properties, were prepared. The "peptisation sol" (so-called from its preparation by peptisation of precipitated cerous hydroxide) is strongly acid, coagulates on warming or on dialysis and also, in a very irregular manner, on addition of electrolytes. Free cerous salt is always present. The "freshly dialysed sol," *i.e.*, that which is viscous and is inclined to gelatinise, has in general the properties described by Fernau and Pauli (A., 1917, ii, 189). It is hydrated and con-

tains nitric acid as the peptising electrolyte; its properties are influenced by the escape of nitric acid from the dialyser and the entry of water. Addition of alcohol results in the replacement of water with formation of alcohol-gels. The "altered sol," one that has lost its viscosity by long keeping, behaves differently towards electrolytes, although no change has taken place in the proportions of ter- and quadri-valent cerium. This sol appears from a detailed study of its viscosity to be non-hydrated, yet the coagulation values indicate the influence of ion-lyotropy. From the viscosity experiments, reasons for the spontaneous congelation of the authors' sols as contrasted with the non-congelation of those prepared by Fernau and Pauli (*loc. cit.*) are adduced. H. J. E.

The Conversion of Aluminium-Zinc Alloys into a Crystalline Form. ALEXANDER SEMENOVITSCH FEDOROV (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 394—407).—A binary fusion diagram is constructed for mixtures of aluminium and zinc. The diagram obtained corresponds with those of Shepherd (A., 1905, ii, 588) and of Eger (A., 1913, ii, 408), who found no evidence for the formation of the alloy Al_2Zn_3, which Rosenhain and Archbutt (A., 1911, ii, 895) observed to occur within the limits 5—22% of aluminium. Photomicrographs of certain of the alloys also indicate that no compound formation occurs. R. T.

The Corrosion of Iron in Presence of Iron Sulphide. ROBERT STUMPER (*Compt. rend.*, 1923, **176**, 1316—1317).—The effect of iron sulphide on the corrosion of iron was investigated under different conditions, the results showing that corrosion was considerably increased in the case of direct contact of iron with the sulphide, whilst in the case of galvanic contact the corrosion was more than twice as great. The general conclusion is drawn that the phenomenon is electro-chemical. H. J. E.

The Physico-chemical Investigation of Ternary Alloys of Iron, Phosphorus, and Carbon. III. -IV. Electrical Conductivity and Hardness. N. S. KONSTANTINOV (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 311—334).—The electrical conductivity curve of the binary system, iron-phosphorus, corresponds with the fusion curve, and indicates the existence of solid solutions of the components up to the saturation concentration of 1·75% of phosphorus, after which a phase corresponding with an alloy, Fe_3P, separates. The hardness of the alloys increases linearly up to the saturation point for solid solution, at which a break occurs in the curve, the degree of hardness continuing to rise more slowly in the eutectic regions. With ternary iron-phosphorus-carbon alloys, the electrical conductivity depends on the carbon content, the addition of the same quantity of phosphorus to iron containing 0·7% of carbon causing a greater increase in resistance than when the carbon content is 0·4%. The hardness of the alloys varies in a parallel way to the conductivity, but to a less marked extent. The effect of the addition of phosphorus to steels is less marked when they are tempered than when they are allowed to cool slowly.

The presence of free phosphorus in the binary and ternary alloys can be shown by treating their polished surfaces with 10% sodium carbonate solution, and in this way it is shown that all eutectic alloys containing from 0—1·2% of carbon and from 0—1·9% of phosphorus are binary phosphorus-iron eutectics. R. T.

Alloys of Iron and Aluminium. N. KURNAKOV, G. URAZOV, and A. GRIGORIEV (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 270—293).—The freezing points, the micro-structure, and the electrical conductivities of alloys of iron and aluminium, ranging from 0 to 100% of each constituent, are investigated. The components of such alloys are, in general, aluminium, occurring to a preponderating extent in the aluminium eutectic mixture, an alloy called δ-alloy, and solid solutions of aluminium in α- and γ-iron. A compound, Al_3Fe_2, crystallises from molten mixtures containing from 32·1 to 39·5 atomic % of iron, but below 1100° this is unstable, and changes into a solid solution of aluminium in α- and γ-iron, and for this reason cannot be found in the solid alloy. The δ-alloy exists within the limits of 24·2—34 atomic % of iron. This alloy is distinguished from others by its brittle nature, its hardness, this being several times greater than that of any other alloy, by its minimum values for electrical conductivity, and for its temperature coefficient of electrical resistance. The constituents of this alloy are not in any simple relation to one another, so that it appears to be, not a definite chemical compound, but probably a double compound of the Berthelot type (cf. *ibid.*, 1912, **44**, 107) in which two or more aluminium-iron compounds, themselves unstable, form a solid solution, stable within the concentration limits above mentioned. R. T.

Iron Oxide Jellies. (FRL.) E. SCHALEK and A. SZEGVARY (*Kolloid Z.*, 1923, **32**, 318—319).—Transparent, slightly elastic ferric oxide jellies may be produced by adding sodium sulphate or sodium chloride to a 6—10% ferric oxide sol. The amount of electrolyte added must be insufficient to cause coagulation. On shaking the jellies gently, they reassume the liquid form, but on keeping, the liquefied jelly sets again, producing a mass identical in every way with the original jelly. This process may be repeated indefinitely without changing the nature of the jelly ultimately obtained. J. F. S.

Nickel Sulphide. W. GLUUD and W. MÜHLENDYCK (*Ber.*, 1923, **56**, [*B*], 899—901).—In extension of Gluud's experiments on copper sulphide (A., 1922, ii, 446, 572), the authors have examined the behaviour of other sulphides which are soluble in ammonia, notably those of zinc, cadmium, cobalt, manganese, and nickel. Of these, only that last named shares the ability of copper sulphide to yield free sulphur when its solution is oxidised by air. The concentration of the ammonia and the age of the sulphide appear to influence the course of the change to a less extent with nickel than with copper sulphide. H. W.

Oxidation of Nickel Sulphide. JOHN STANLEY DUNN and ERIC KEIGHTLEY RIDEAL (T., 1923, 123, 1242—1251).

Theory of Smelting. III. Equilibrium between Metal Pairs and Sulphur. The System Nickel–Antimony–Sulphur. W. GUERTLER and H. SCHACK (*Metall u. Erz*, 1923, 20, 162—167).—In the ternary system nickel-antimony-sulphur there are four binary compounds, Ni_5Sb_2, NiSb, Ni_3S_2, and NiS, that melt unchanged and one ternary, NiSbS. All these compounds form binary eutectics among themselves, and there is also evidence of a ternary eutectic consisting principally of NiSbS and NiS. The complete ternary diagram of the system is reproduced, as well as photographs showing the characteristic structure of certain of the alloys (cf. *J.S.C.I.*, 1923, June). A. R. P.

Reduction by Hydrogen of Metallic Oxides Reducible only with Difficulty. H. VON WARTENBERG, J. BROY, and R. REINICKE (*Z. Elektrochem.*, 1923, 29, 214—217).—A simple form of electrically-heated furnace suitable for heating substances to temperatures up to 2500°, in the presence of hydrogen or nitrogen under pressures up to 10 atmospheres, is described. The substance to be heated is contained in a tube of zirconium oxide or of 80% zirconium oxide and 20% yttrium oxide, or of thorium oxide, heated by current flowing through a spiral of tungsten wire wound round the tube. In the case of the reduction of oxides in the presence of hydrogen, water formed is absorbed by means of phosphoric oxide. Chromium oxide (Cr_2O_3), vanadium oxide (V_2O_3), and columbium oxide (Nb_2O_5) were reduced in hydrogen at a pressure of about 5 atmospheres. The authors were unable to reduce tantalum oxide (Ta_2O_5), titanium oxide (TiO_2), or uranium oxide (UO_2). The oxides of yttrium, zirconium, and thorium could be similarly reduced by hydrogen in the presence of another metal, *e.g.*, tungsten, with which the reduced metal alloyed. At 1250°, tungsten dissolved 0·07% of thorium, whilst at 2000° the saturation solubility of thorium in tungsten was 0·24%. The solubility was not much affected by the presence of iron, but was considerably reduced when zirconium was present. The question as to whether thorium contained in tungsten filaments used in electric incandescence lamps exists as metal or oxide cannot be decided by analysis alone.
J. S. G. T.

Basic Chromic Sulphate. F. S. WILLIAMSON (*J. Physical Chem.*, 1923, 27, 384—388).—The production of basic chromic sulphates has been investigated. It is found that by adding 2—5 g.-mols. of sodium hydroxide to 1 g.-mol. of potassium chromium alum a precipitate is obtained which has practically a constant composition, and it must therefore be tentatively regarded as a definite basic salt of the formula $(Cr_2O_3)_7(SO_3)_5,25H_2O$. At the ordinary temperature, the salt is practically stable when kept over concentrated sulphuric acid. On heating the compound to 150°, it lost 36% of the total water, at 200° the loss of water was 64% of the total, and at 250° the whole of the water except about

5% was expelled. The loss of water is not reversible. These facts make it extremely unlikely that the water contained in the salt is present as water of crystallisation. Material which has been heated at 250° when moistened with water takes up only a small fraction of the water lost. The present basic salt retains its water more vigorously than the corresponding basic aluminium sulphate previously described (this vol., ii, 324). J. F. S.

The Oxidising Properties of Sulphur Dioxide. IV. Molybdenum Sulphates. WILLIAM WARDLAW and NORMAN DARBY SYLVESTER (T., 1923, **123**, 969—980).

Crystal Structure of Tin Tetraiodide. ROSCOE G. DICKINSON (*J. Amer. Chem. Soc.*, 1923, **45**, 958—962).—The crystal structure of stannic iodide has been investigated by means of *X*-ray and Laue photographs. It has been found that the unit cube contains eight molecules of stannic iodide; the value of d^{100} is found to be 12·23 Å. The iodine atoms cannot be all in equivalent positions. The space group symmetry is T_h^6. It is shown to be probable that the tin atoms are at points equivalent to (*uuu*) and the iodine atoms at points equivalent to (*vvv*) and (*xyz*). The values $u=0{\cdot}129$, $v=0{\cdot}253$, $x=0{\cdot}009$, $y=0{\cdot}001$, and $z=0{\cdot}253$ have been found to account for the intensity data, and to surround each tin atom tetrahedrally by iodine atoms. If these parameters are even approximately correct, the structure may be considered to be molecular. J. F. S

Eutectic Mixtures of Stannic Iodide with Iodine, Arsenic Tri-iodide, and Antimony Tri-iodide. A. M. VASILIEV (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 88—91; cf. A., 1912, ii, 919).—Stannic iodide shows practically no tendency to form double compounds, and it was to be expected that simple eutectics would be obtained, as already observed for stannic iodide and iodine by van Klooster (A., 1913, ii, 142) and by Reinders and de Lange (A., 1913, ii, 60). This was found to be the case.

The system stannic iodide–iodine was reinvestigated, using the freezing-point method; the eutectic point was found to be 77·8° and the composition corresponded with $SnI_4+3{\cdot}257\,I$, in good agreement with the published values (see above).

The eutectic of stannic iodide with arsenic tri-iodide melts at 106·2° and solidifies to a brick-red, amorphous mass, its composition being $AsI_3+0{\cdot}6936\,SnI_4$.

The eutectic of stannic iodide and antimony iodide is a dark red, crystalline solid, melting at 127° and having the composition $SbI_3+0{\cdot}8728\,SnI_4$. G. A. R. K.

The Behaviour of Stannic Acid towards Dyes. A. M. MORLEY and J. K. WOOD (*J. Soc. Dyers and Col.*, 1923, **39**, 105—106).—Samples of stannic acid obtained by precipitation from an alkaline solution adsorb basic dyes, whilst those from a slightly acid solution adsorb acid dyes. This behaviour is similar to that of different samples of titanic acid (following abstract) and may be explained in a similar manner. E. H. R.

The Behaviour of Titanic Acid towards Dyes. A. M. MORLEY and J. K. WOOD (*J. Soc. Dyers and Col.*, 1923, **39**, 100—105).—It is generally supposed that meta- or β-titanic acid differs from ortho- or α-titanic acid in the greater complexity of its ultimate particles. The greater relative surface of the α-form might be expected to result in its having a greater adsorptive capacity than the β-form. Experiments on the adsorption of dyes by different forms of titanic acid have confirmed this deduction, for α-titanic acid, prepared by adding ammonia to a cold solution of titanic chloride until alkaline, had a greater adsorptive power for basic dyes than the β-acid precipitated in a similar manner at the boiling point. These preparations did not adsorb acid dyes, but samples obtained by stopping the precipitation while the solution was still acid adsorbed acid dyes readily, but not basic dyes. Finally, samples of titanic acid obtained by precipitation of a solution of titanic chloride with calcium carbonate had a very much lower adsorptive power, but took up both acid and basic dyes to a small extent. The difference in behaviour of titanic acid obtained from acid and alkaline solutions, respectively, may be attributed to the amphoteric character of titanium hydroxide, resulting in the formation in the one case of a highly basic titanium salt, and in the other of an alkali titanate; or it may be accounted for by the adsorption of hydrogen- or hydroxyl-ions, giving positively and negatively charged colloidal particles, respectively. Titanic acid obtained by precipitation with calcium carbonate would be neutral and have no preference for negative or positive ions of basic or acidic dyes. E. H. R.

Urbain's Celtium Lines. H. M. HANSEN and S. WERNER (*Nature*, 1923, **111**, 461).—In view of a previous observation that the optical spectrum of hafnium does not contain any of the lines belonging to the characteristic spectrum ascribed by Urbain to a rare-earth element celtium, an examination has been made of the measurements of the spectra of rare earths published by Eder, and it is noted that the majority of Urbain's celtium lines (A., 1911, ii, 115) have been observed (Eder, A., 1916, ii, 277) in the spectrum of lutecium. The optical spectrum of a very pure preparation of lutecium has been reinvestigated, and it is found that the conditions affecting the relative intensities of the lines lead to the assumption that Urbain's preparation contained a comparatively small amount of the element with atomic number 71, and that only after further treatment of the preparation a concentration was obtained sufficient for the production of the diffuse lines which in 1911 were ascribed to the presence of a new element celtium. The *X*-ray spectrum of the same pure preparation gave no indication of the presence of an element with atomic number 72. A. A. E.

Celtium and Hafnium. D. COSTER and G. HEVESY (*Nature*, 1923, **111**, 462—463; cf. preceding abstract, and Urbain, this vol., ii, 171).—The development of the controversy regarding the existence of an element with the properties ascribed to celtium is briefly reviewed, and it is argued that the magnetic properties

observed by Urbain in his preparations of 1911 need not be explained as being due to the presence of a new element, but may be considered to be a consequence of the gradual concentration of lutecium (Auer von Welsbach's cassiopeium) in his preparations. Moreover, hafnium can be readily separated from the rare-earth elements by means of oxalic acid, and should therefore have been absent from Urbain's preparation in which Dauvillier considered an element of atomic number 72 to be present. The claim to the identity of celtium with hafnium, and consequent priority of nomenclature, is therefore rejected. A. A. E.

The Chemistry of Thorium. V. I. SPICIN (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 357—370).—The solubilities of various difficulty soluble thorium salts in various acids and alkalis and in water are measured by a modification of a method described by Joly (A., 1909, ii, 458), which consists of the addition of a small quantity of a strongly radioactive isotope of thorium to a solution of the latter, and precipitating them together, the solubility being then measured by boiling the salt in the given reagent, and measuring the radioactivity of the saturated solution. Joly did this by passing the emanation into a gold-leaf electroscope, obtaining results accurate to within 10%. By more carefully regulating the speed of the current of air passed over the solution for the purpose of collecting emanation, an accuracy of 1—2% is obtained. A different method based on a similar principle is also used, this consisting of the measurement of the β-radiation of isotopic mixtures of salts of thorium and of uranium-X_1, prepared as in Joly's method. Portions of the solutions of these salts are then evaporated to dryness, and the β-radioactivity of the residue is compared with that of the original mixture. The accuracy of this method is also 1—2%. The advantages of this over Joly's method are that determinations can be carried out immediately, whilst for the latter method it is necessary to wait one month for equilibrium conditions, and further that the technique of the operations involved is not so difficult, the analysis requiring three and a half hours instead of five. This method cannot, however, be applied to the estimation of thorium in solutions containing non-volatile mineral substances, such as sodium hydroxide. R. T.

Crystal Structures of the System: Palladium-Hydrogen. L. W. MCKEEHAN (*Physical Rev.*, 1923, [ii], **21**, 334—342).—The system: palladium-hydrogen has been studied by measuring the changes in crystal structure produced by the process of occlusion. The parameters of the face-centred cubic lattices of palladium and palladium saturated with hydrogen, as measured by the usual powder method, employing the *K*-radiation of molybdenum filtered through zirconium oxide, were found to be 3·900 and 4·000–4·039 $\times 10^{-8}$ cm., respectively. A value of 4·036 $\times 10^{-8}$ would correspond with a compound Pd_2H, but it is pointed out that the variability in the parameter of saturated crystals is opposed to the assumption of the formation of a definite compound in every case. Only two crystalline phases appear to coexist, namely,

palladium and a saturated solution of hydrogen in palladium; with partly saturated strips of metal, the distribution of saturated crystals over the surface was shown to be irregular. Further, the presence of atomic hydrogen, produced by electrolysis of dilute sulphuric acid with a palladium electrode, or by surface dissociation of hydrogen at high temperatures, is a necessary condition of occlusion. The paper concludes with the compilation of a number of physical assumptions concerning the nature of the system, with which the phenomena observed appear to be consistent; a bibliography of recent literature is also appended. A. A. E.

The Crystal Structure of Silver-Palladium and Silver-Gold Alloys. L. W. McKeehan (*Physical Rev.*, 1922, **20**, 424—423).—The *K*-radiation of molybdenum was allowed to fall on the face of a thin ribbon of silver, gold, or palladium, and of seven binary alloys in each of the series of silver–gold and silver–palladium alloys, the shadow cast by the edge of the ribbon, and the diffracted beams due to its suitably oriented crystals being detected by a strip of photographic film wrapped on a cylinder, the axis of which coincides with the edge of the ribbon. All the metals and alloys examined have their atoms arranged in face-centred cubic lattices with unit edge of cube $4{\cdot}08\times10^{-8}$, $4{\cdot}075\times10^{-8}$, and $3{\cdot}90\times10^{-8}$ cm. for silver, gold, and palladium, respectively. For both series of alloys (except in the case of silver–gold alloys containing 30, 40, and 60% of silver, which gave results 1% too high), the length of the edge is nearly a linear function of the atomic percentage of either component. Annealing at 830—940° in a vacuum for at least an hour increased the size of individual crystals, rendered them more homogeneous, and made their orientations more isotropic, whereas moderate cold working reduced their size and made them less isotropic. In the case of the silver–palladium alloy when repeatedly annealed at 870°, no indication of a progressive change of composition could be detected; the volatility of silver at this temperature is therefore negligible. The densities of crystals of silver, gold, and palladium are computed to be 10·49, 19·24, and 11·87, respectively. A. A. E.

Mineralogical Chemistry.

The Relative Chlorine, Bromine, and Iodine Content of the Waters of the Strait of Georgia, B.C. A. T. Cameron (*Contrib. Canad. Biol.*, 1922, 75—80).—By the use of Winkler's methods (A., 1916, ii, 109, 184, 389), the relative proportions of chlorine, bromine, and iodine present in the water examined were 100 : 0·358 : 0·0002, as compared with 100 : 0·347 : 0·00023 found by Winkler for the Adriatic. As reported by Winkler, most of the iodine was present as iodate. Chemical Abstracts.

Analytical Chemistry.

Modification of Gillespie's Method for the Determination of Hydrogen-ion Concentrations. WILLIAM D. HATFIELD (*J. Amer. Chem. Soc.*, 1923, **45**, 940—943).—Gillespie's method for the determination of hydrogen-ion concentration has been investigated, and a modified procedure is put forward (A., 1920, ii, 382). The modifications consist essentially in the method of preparing the indicator solutions and the buffer solutions, details of which are given in the paper. The standards prepared have been preserved from four to eight weeks or more. The method as modified is particularly suited to average technical laboratory practice because of its accuracy, simplicity of technique, and the use of ordinarily pure reagents instead of the specially purified materials recommended by Clark. J. F. S.

The Nephelometer and its Working. HANS KLEINMANN (*Biochem. Z.*, 1923, **137**, 144—156).—The criticisms of Weinberg (A., 1922, ii, 309) of the Kleinmann nephelometer (A., 1920, ii, 634) are replied to. A modified apparatus is now described suitable for small quantities of liquid, 2·6 or 1·5 c.c., and a method of producing permanent standards is described. A matt appearance is produced by coating a tube with collodion containing talc in suspension, colour variations of the turbidity being obtained by use of a separate powder containing talc, copper sulphate, and litmus powder in suitable proportions. With the Kleinmann nephelometer as now made a somewhat modified permanent standard of turbidity is used. H. K.

The Use of the Oxy-acetylene Blowpipe in Spectral Analysis. Application to Mineralogy. A. DE GRAMONT (*Compt. rend.*, 1923, **176**, 1104—1109).—A description is given of the application of the oxy-acetylene blowpipe flame in the spectral analysis of certain minerals. The method and apparatus employed are similar to those already described for the case of aluminium (A., 1914, ii, 82), and whilst the oxy-acetylene flame has not the universal applicability of the spark spectrum, it can be successfully used for the alkali and alkaline-earth metals, copper, silver, gallium, indium, thallium, chromium, manganese, iron, cobalt, nickel, tin, lead, and bismuth, and somewhat less satisfactorily for magnesium, zinc, cadmium, and mercury. A reproduction of the spectra of hæmatite, chromite, and lepidolite obtained by this method is given. G. F. M.

Systematic Method for the Detection of the Principal Anions. L. FERNANDES and U. GATTI (*Gazzetta*, 1923, **53**, i, 108—114).—According to the scheme proposed by the authors, the principal anions are precipitated by a number of successive group reagents, each precipitate being then tested for the possible anions. *Group I*: Magnesium nitrate and ammonia solution precipitate carbonic, phosphoric, phosphorous, arsenic, arsenious,

hydrofluoric, silicic, and hydroferrocyanic acids. *Group II*: Calcium and ammonium nitrates precipitate sulphurous, molybdic, tungstic, oxalic, tartaric, and citric acids. *Group III*: Barium nitrate precipitates sulphuric, chromic, and thiosulphuric acids. *Group IV*: Mercuric nitrate precipitates hydroferricyanic and vanadic acids. *Group V*: Silver nitrate precipitates hydrochloric, hydrobromic, hydriodic, and thiocyanic acids. *Group VI*: The residual liquid is tested for hydrocyanic, boric, hypophosphoric, chloric, perchloric, nitrous, benzoic, and salicylic acids. Separate tests are made for nitric, carbonic, and acetic acids, the last two being introduced, prior to the group precipitations, by fusion of the substance with sodium carbonate and decomposition of excess of the carbonate by means of acetic acid. T. H. P.

Direct Estimation of Oxygen in the Gaseous Exchanges of Animals. K. I. Godzikovski and A. A. Lichatschev (*J. Russ. Physiol.*, 1918, **1**, 56—60).—The method is based on that of Regnault and Reiset. The arrangement of the apparatus employed by the authors is illustrated diagrammatically in the original. E. S.

Titration of Sulphates. Erwin Benesch (*Chem. Ztg.*, 1923, **47**, 366).—The sulphate is precipitated with excess of barium hydroxide and the excess precipitated with ammonium carbonate, which is then removed by boiling and the alkali carbonate titrated. The results obtained agree well with gravimetric determinations, and the determination can be completed in two hours. If the sulphate solution contains a kation the hydroxide or carbonate of which is insoluble, the kation is precipitated with sodium hydroxide, filtered, and the filtrate neutralised with hydrochloric acid before the barium hydroxide is added. H. C. R.

Electrometric Titration of Selenium in the Presence of Tellurium, Iron, and Copper. H. H. Willard and Florence Fenwick (*J. Amer. Chem. Soc.*, 1923, **45**, 933—939).—The volumetric estimation of selenium by means of titanous sulphate solution has been investigated. It is shown that the volumetric reduction of selenious acid to selenium by titanous sulphate in hydrochloric acid solution saturated with sodium chloride is rapid and accurate in cold solutions to 0·1 mg. Under these conditions, tellurium is not reduced, and its only effect is to modify the nature of the end-point. Moderate amounts of sulphuric acid have no deleterious effect on the determination of the end-point, and there is no volatilisation of selenium at the fuming temperature of this acid. The titration of selenium is quantitatively independent of the concentration of any iron which may be present, although ferrous iron is produced in the reaction. The reducing effect of tervalent titanium on mixtures containing copper and selenium is selective, the latter being reduced first, and consequently both elements may be determined electrometrically in a single titration. J. F. S.

Use of Hydrogen Peroxide in the Estimation of Nitrogen. Robert Heuss (*Woch. Brau.*, 1923, **40**, 73—74).—The use of

hydrogen peroxide, as suggested by Kleemann (*Z. angew. Chem.*, 1921, **34**, 625) in Kjeldahl's method for estimating nitrogen, is of advantage in the case of barley, the time required for the complete attack of 1·75 g. of the finely-ground grain being reduced from seventy-five to ninety minutes to forty-five minutes. The quantities of the different reagents suggested by Kleemann may be reduced to: 7—8 g. of potassium sulphate, 20 c.c. of sulphuric acid, and 15 c.c. of 30% (by weight) hydrogen peroxide solution. A blank estimation must be made with the materials alone and the results corrected accordingly. T. H. P.

Use of Persulphate in the Estimation of Nitrogen. I, By the Arnold-Gunning Modification of Kjeldahl's Method; II, by Folin's Direct Nesslerisation Method. SAN YIN WONG (*J. Biol. Chem.*, 1923, **55**, 427—430, 431—435).—I. Considerable saving of time results if the following procedure is adopted: When the acid mixture becomes amber-coloured, heating is discontinued. Water (3 c.c.) and potassium persulphate (10 g.) are added and the mixture is again heated until oxidation is complete.

II. This modification has been adapted to Folin's direct nesslerisation method for the estimation of nitrogen in urine, blood, and milk. E. S.

Estimation of Nitrogen in Aromatic Nitro-compounds by the Kjeldahl-Flamand-Prager Method. B. M. MARGOSCHES and W. KRISTEN (*Z. ges. Schiess.-Sprengstoffw.*, 1923, **18**, 39—40).—The Kjeldahl-Flamand-Prager method (A., 1905, ii, 201) for estimating nitrogen in azo-compounds can be applied to aromatic mono-, di-, and tri-nitro-compounds with good results, except in the cases of dinitrotoluene, dinitroxylene, trinitroresorcinol, and nitrotoluidine, which showed errors up to −3%, and nitrotoluene and nitrobenzyl chloride, which showed errors up to −12%. The error in most cases does not exceed 1%. The method has certain advantages over other modifications of the Kjeldahl method, particularly as regards rapidity. H. C. R.

Detection of Hydroxylamine. WALDEMAR M. FISCHER (*Chem. Ztg.*, 1923, **47**, 401).—A sensitive colour reaction capable of detecting hydroxylamine in a concentration of 0·00005%, is carried out by adding 1—2 drops of 2½% yellow ammonium sulphide solution, and 1—2 c.c. of ammonia to 1—5 c.c. of the solution to be tested. In presence of hydroxylamine an unstable purple colour is developed in the solution on shaking in presence of air, and its appearance is greatly accelerated by adding 1—2 drops of $N/10$-manganous sulphate solution which appears to act as an oxidising catalyst. The reaction is apparently specific for hydroxylamine, and it is not disturbed by the presence of ammonium or hydrazine salts, or by any of the common anions or kations with the exception of those giving insoluble precipitates with hydrogen sulphide in acid solution, which must first be removed by filtration. The nature of the purple colour is uncertain, but it may be due to the formation of a bivalent sulphur compound or of a sulphur dispersion. G. F. M.

New Test for Nitrates. IVOR G. NIXON (*Chem. News*, 1923, **126**, 261—262).—β-Naphthol-6 : 8-disulphonic acid ("G acid"), 7-amino-α-naphthol-3-sulphonic acid ("Gamma acid"), 1 : 6- and 1 : 7-naphthylaminesulphonic acids ("Cleve's acids") all react vigorously with solutions of nitrates and nitrites, giving wine-red solutions. With "G acid" a distinct red colour was obtained with 0·02 mg. of nitrogen as nitric acid. 1 C.c. of the suspected solution is mixed with 1 c.c. of concentrated sulphuric acid and 5 c.c. of a 1% solution of "G acid" is slowly added. The test may also be applied as a ring test if the nitrate solution is mixed with the sulphonic acid, and concentrated sulphuric acid is run down the side of the test-tube. There is no need to cool the solutions during the test.
H. C. R.

Gravimetric Estimation of Organic Phosphorus. WALTER JONES and M. E. PERKINS (*J. Biol. Chem.*, 1923, **55**, 343—351).—The substance is oxidised as in Kjeldahl's nitrogen method, and the phosphorus precipitated from the diluted digest as ammonium phosphomolybdate. The latter is dissolved in ammonia and the solution so obtained treated at the boiling point, drop by drop, with magnesia mixture. After cooling, one-third of its volume of concentrated ammonia is added, and the mixture left overnight. Under these conditions, the precipitate of magnesium ammonium phosphate forms large, stable crystals of constant composition ($MgNH_4PO_4,6H_2O$). After filtering and drying in the air, these can be readily removed quantitatively from the filter-paper and hence may be weighed in this form without conversion into the pyrophosphate. Similar large crystals of magnesium ammonium phosphate may be obtained from solutions of phosphates if the precipitation is made in the presence of ammonium molybdate.
E. S.

The Analysis of Glasses Rich in Boric Oxide. VIOLET DIMBLEBY and W. E. S. TURNER (*J. Soc. Glass Tech.*, 1923, **7**, 76—79).—In the estimation of boric oxide in glass by the method described by Cauwood and Wilson (A., 1919, ii, 169), boric oxide is lost by volatilisation during the sodium carbonate fusion unless the glass does not contain much more than 10% of B_2O_3. It is therefore recommended, in the analysis of glasses rich in boric oxide, to reduce the amount of glass taken for analysis and to add pure silica to adjust the boric oxide content to about 10%. The weight of sodium carbonate for a fusion is kept constant at 3 g. and the combined weight of glass and silica is adjusted accordingly.
E. H. R.

Estimation of Carbon and Hydrogen by Means of a Mixture of Sulphuric Acid and Silver Dichromate. L. J. SIMON and A. J. A. GUILLAUMIN (*Compt. rend.*, 1923, **176**, 1065—1067).—Numerous substances which are not completely burnt by a chromic-sulphuric acid mixture, give satisfactory results with silver dichromate and sulphuric acid. A known weight, *p*, of the substance is heated at 100° with a weighed excess, *P*, of silver

dichromate (about 6 g.) and sulphuric acid for twenty minutes. From the volume of carbon dioxide produced, or the increase in pressure, the weight, π, is obtained and the percentage of carbon is given by $300\pi/11p$. The hydrogen is obtained by a second combustion with the residue and an excess of an easily combustible substance such as potassium methyl sulphate. If α is the weight of carbon dioxide corresponding with 1 g. of $Ag_2Cr_2O_7$, and π' the weight of carbon dioxide evolved in the second combustion, π'/α is the weight of dichromate present and the residue from the first combustion, and $P-\pi'/\alpha$ is the weight used in that combustion. The percentage of hydrogen is then given by $[9(p-\pi)+P-\pi'/\alpha]100/81p$. The value of α determined empirically is 0·108, the difference from the theoretical, 0·102, being due to the production of small amounts of carbon monoxide when the dichromate is not present in excess. The results of analyses by this method of naphthalene, strontium acetate, ethyl pyruvate, rhamnose, aspirin, thymol, etc., are quoted. G. F. M.

Analysis of Potassium Iodide. H. MATTHES and P. SCHÜTZ (*Pharm. Ztg.*, 1923, 68, 256—257).—The following method is recommended for the estimation of potassium iodide in the presence of bromides and chlorides. One g. of the dry powdered salt is dissolved in water and the solution diluted to 100 c.c.; 10 c.c. of this solution are treated in a stoppered flask with 5 c.c. of 2% sodium nitrite solution and 2 c.c. of dilute sulphuric acid. After five minutes, 100 c.c. of 5% sodium hydrogen carbonate solution are added slowly and the liberated iodine is titrated with $N/50$-arsenic trioxide solution. Each c.c. of the latter is equivalent to 0·00332 g. of potassium iodide. W. P. S.

Nephelometric Estimation of Small Quantities of Calcium. P. RONA and H. KLEINMANN (*Biochem. Z.*, 1923, **137**, 157—182).—For the estimation of small quantities of calcium, as, for instance, in blood, the Kleinmann nephelometer or micro-nephelometer is employed. Lyman's reagent, ammonium stearate, for the production of a cloud (A., 1915, ii, 700; 1917, ii, 271) is replaced by sodium sulphoricinoleate. The authors have examined the influence of time, volume, impurities, and degree of alkalinity of the reagents on the production of the cloud. Using the micro-nephelometer, the calcium in 0·25 c.c. of blood can be estimated with a probable error of 1%. H. K.

The Influence of Phosphoric Acid on the Volumetric Estimation of Calcium. J. GROSSFELD (*Chem. Weekblad*, 1923, 20, 209—210).—A criticism of the modifications suggested by Vürtheim and van Bers (this vol., ii, 257) on the procedure of the author. In presence of a large excess of phosphoric acid, neutralisation with ammonia and precipitation with oxalate causes the carrying down of calcium phosphate, which is avoided if the neutralisation is not carried too far, the author's procedure leading to the formation of primary sodium phosphate only. The change in volume due to evaporation consequent on the heat of neutralisation is negligible. S. I. L.

Estimation and Quantitative Separation of Barium and Strontium. Rudolf Leo (*Monatsh.*, 1923, **43**, 567—588).—A careful investigation has been made of a modification of Fresenius's fluorosilicate method for the quantitative separation of barium and strontium, consisting in using ammonium fluorosilicate in place of the free acid; in addition, a method for separating barium and strontium by means of their thiosulphates has been developed, which gives satisfactory results when there is a relatively large excess of barium.

The ammonium fluorosilicate method :—The following points were noticed: (1) the solubility of barium fluorosilicate is depressed by using ammonium fluorosilicate in place of the free acid so that precipitation is more nearly quantitative. (2) Barium fluorosilicate dried at 180° to constant weight gives results 0·2 to 0·3% too high, due to water. (3) Heating barium fluorosilicate in an electric oven for two to three hours only converts it incompletely into barium fluoride. (4) Barium precipitated by ammonium fluorosilicate in neutral or acetic acid solution always carries down some strontium; this can be counteracted by the addition of hydrochloric acid. (5) Barium precipitated from hot solution carries down more strontium than when precipitated from cold solution. (6) The decomposition of barium and strontium fluorosilicates by means of excess of warm ammonia and ammonium carbonate takes place completely in about ten minutes, and can be utilised for the complete separation of barium and strontium.

The analysis is effected in the following manner: 50—70 c.c. of a solution of 0·3 to 0·5 g. mixed barium and strontium chlorides are treated with 6—10 c.c. of *N*-hydrochloric acid per 100 c.c. and with a 10—50% excess of a 10% ammonium fluorosilicate solution. After thirty minutes, $\frac{1}{3}$ volume of alcohol is added. The washed and decanted precipitate is then warmed with excess of ammonia and ammonium carbonate. The granular precipitate of barium carbonate is dissolved in dilute hydrochloric acid and the barium fluorosilicate reprecipitated as before. The precipitate is finally converted into barium sulphate by heating with sulphuric and hydrofluoric acids. The strontium left in the filtrates is determined as sulphate.

The thiosulphate method :—The solubility of barium thiosulphate in water at 18·5° is 1 in 479·8, and in a mixture of equal volumes of acetone and water, 1 in 31,450, the solubility of strontium thiosulphate in the mixed solvent at 18·5° being 1 in 281·7. The following special points were noted: (1) A slight excess of sodium thiosulphate diminishes considerably the solubility of barium thiosulphate, which, however, carries down some sodium salts. (2) By reprecipitating the barium as barium thiosulphate, satisfactory results are obtained if there is a large excess of barium over strontium; in the converse case, the precipitated barium thiosulphate always contains some strontium. In carrying out the estimation, the solution of the mixed chlorides of barium and strontium is treated with a slight excess of sodium thiosulphate with stirring, an equal volume of acetone added, and the mixture

allowed to remain. The washed and decanted precipitate is dissolved in hydrochloric acid, the solution concentrated, and the barium reprecipitated as thiosulphate, which is then redissolved in hydrochloric acid and estimated as sulphate. The filtrates containing strontium are concentrated, and the strontium estimated as sulphate. F. A. M.

Volumetric Estimation of Manganese as "Permanganic Phosphate" in Phosphoric Acid Solution. MATHEVET (*Ann. Chim. Analyt.*, 1923, **5**, 99—108).—The substance is dissolved in a mixture of phosphoric, nitric, and sulphuric acids and silver nitrate is added as a catalyst together with ammonium persulphate. A violet-amethyst coloration appears, and the liquid is titrated with arsenious acid. The end-point is sharper in the presence of phosphoric acid, and there is less danger of precipitates being formed. The presence of iron does not disturb the titration, as the colour of the iron salts is destroyed by the phosphoric acid. The mechanism of oxidation with ammonium persulphate is discussed. The mode of action of the phosphoric acid is uncertain. The use of nitric acid alone gives higher results than a nitric-sulphuric acid mixture, some arsenious acid probably being oxidised by the nitric acid. The results are not sensitive to the amount of phosphoric acid present, unless it is in large excess. In titrating solutions rich in manganese, sufficient phosphoric acid must be present to obtain all the manganese as "permanganic phosphate" and sufficient sulphuric acid to transform the manganese reduced during the titration into sulphate. Details are given for the application of the method to the analysis of cast irons, manganese steels, and alloys containing chromium, nickel, copper, cobalt, molybdenum, and vanadium. The manganese in an ordinary steel can be determined by this method in about seven minutes. H. C. R.

Quantitative Separation of Manganese and Chromium. H. J. TAVERNE (*Chem. Weekblad*, 1923, **20**, 210—211).—The metals are precipitated with ammonium sulphide and redissolved in water after conversion into chlorides; the solution is treated with hydrogen peroxide and sodium hydroxide, and boiled for thirty minutes; manganese is collected as hydrated oxide and weighed as sulphate, the chromate in the filtrate being titrated by means of iodine.

S. I. L.

Colorimetric Estimation of Iron and Hæmoglobin in Blood. SAN YIN WONG (*J. Biol. Chem.*, 1923, **55**, 421—425).—One c.c. of blood is used for the estimation. Organic material is oxidised by heating with concentrated sulphuric acid (1 c.c.) for three and a half minutes, carefully adding 1 c.c. of a 10% sodium chlorate solution and again boiling for three minutes, and finally boiling for two minutes after the further addition of 0·3 c.c. of the chlorate solution. Iron is then estimated colorimetrically by means of a solution of thiocyanate (cf. Brown, A., 1922, ii, 319). E. S.

New Method for Estimating Nickel. W. LÖFFELBEIN and J. SCHWARZ (*Chem. Ztg.*, 1923, **47**, 369—370).—Nickel may be

precipitated quantitatively from a neutral solution containing only alkali metals and a little ammonia with oxalic acid. This precipitate may either be ignited and weighed as NiO, or dissolved in hot sulphuric acid solution and titrated with permanganate. Details of each method are given, together with specimen analyses, which indicate that both methods are capable of the highest accuracy. The completeness of the precipitation of the oxalate is such that the filtrate only gives a trace of precipitate when boiled for half an hour with dimethylglyoxime; the precipitate is coarser and easier to filter if formed in the presence of ammonium nitrate. It is soluble in strong mineral acids, but not in glacial acetic acid, which, however, makes it slimy and difficult to wash. It is unaffected by excess of oxalic acid or by dilute tartaric, citric, boric, or phosphoric acids. H. C. R.

Electrometric Titration of Molybdenum with a Titanous Salt. H. H. WILLARD and FLORENCE FENWICK (*J. Amer. Chem. Soc.*, 1923, 45, 928—933).—Molybdenum in the sexavalent condition is reduced sufficiently rapidly by a titanous salt to the quinquevalent condition to allow of the process being used for the electro-titrimetric estimation of molybdenum, using a bimetallic electrode system. The titration is carried out in hydrochloric acid solution, the most suitable concentration of acid being about 5—10% of concentrated hydrochloric acid. The end-point is characterised by a slight increase in *E.M.F.* when equivalent amounts are present, followed by a decrease when an excess is added. The reaction is only complete in the presence of a small excess of titrating liquid, and this amount, which must be found for the solutions in question, must be used as a correction factor. The method has been used for alkali molybdates, and found to give results accurate to within 0·5 mg. The method furnishes an indirect method for the estimation of phosphorus. The phosphorus is converted into ammonium phosphomolybdate by any of the recognised methods. The precipitate is dissolved in ammonia, filtered to remove any iron, and the acidified solution titrated with titanous sulphate. If the precipitate is very large, it tends to reprecipitate on the addition of acid. This may be prevented by the addition of a few drops of phosphoric acid to the ammoniacal solution, but the character of the end-point is thereby altered. In the cold, there is no voltage drop with excess of the titrating solution. Just before the end-point, the normal rise begins, ceases, then continues with increased velocity just as the equivalent point is passed. If the solution is titrated hot, however, the end-point is perfectly normal and as distinct as in the absence of phosphoric acid. The presence of tungsten does not interfere with the determination, but it makes it quite unnecessary to apply the correction which is necessary in its absence. J. F. S.

Gravimetric and Volumetric Methods for the Estimation of Tin in Alloys. ANTONIN JÍLEK (*Chem. Listy*, 1923, 17, 53—56, 85—87).—The modification of Gerwek's method for the

estimation of tin, described in a previous article (cf. this vol., ii, 186), is shown to give the best results for bearing metals when for alloys containing 14—30% of tin, 0·5 g. is taken, for 30—75% of tin, 0·25 g. is taken, and for 75—100% of tin, 0·15 g. of alloy is used. If smaller quantities are used, low results are obtained owing to incomplete precipitation of the tin, whilst larger quantities give high results, due to adsorption of antimony salts on the stanniphosphate precipitate.

Classen's electrolytic method for the estimation of tin (A. Fischer, "Electroanalytische Schnellmethoden," p. 217) is tested for bearing metals and found to give satisfactory results with a current of 0·5 ampere, for which V is 3·5. This method has the advantage over Czerwek's method and its modification of being more rapid. For type metal containing about 2% of tin, the results obtained by the modification of Czerwek's method are lower than by the iodimetric method, agreement being obtained commencing with alloys containing more than 14% of tin. Below this, better results are obtained by using the unmodified Czerwek solution. R. T.

Estimation of Tin by Means of the Molybdenum-blue Reaction. G. F. Hüttig (*Chem. Ztg.*, 1923, 47, 341—342).—The colour reaction between ammonium molybdate and stannous tin is of too uncertain a nature to be of use in quantitative analysis at ordinary concentrations, as the molybdenum-blue formed is a colloidal solution and its depth of colour depends on many conditions. In very great dilution, however, the depth of colour produced is directly proportional to the amount of stannous-ions present, other conditions being kept constant. The depth of colour formed under the conditions prescribed for colorimetric estimations reaches a maximum after about thirty minutes, and thereafter remains constant for at least ninety minutes, so that there is ample time for comparison with standards previously prepared. Directions are given for the preparation of the molybdate solution, which must be used before molybdic acid begins to separate. The solution of molybdenum-blue used in the colorimeter should not contain more than 30 mg. of tin per litre, or the proportionality between depth of colour and tin content no longer holds. The depth of colour is not influenced by the presence of antimonious chloride, sodium arsenite, sodium arsenate, or zinc salts. The solution for colorimetric estimation is prepared as follows. The hydrogen sulphide in the hydrochloric acid solution containing tin and antimony is boiled off, zinc and further excess of hydrochloric acid are added to the boiling solution, and the reduction is allowed to proceed for about one minute. The solution is then slowly poured through a filter with constant stirring into a mixture of 6 c.c. of the ammonium molybdate solution prepared as described (as used for testing for phosphoric acid), 3 c.c. of $2N$-sodium hydroxide solution, and about 1000 c.c. of water. 0·1 Mg. of tin is easily detected in the above manner. If antimony alone is present, the solution may show a faint green coloration, which cannot be confused with the blue colour of the tin reaction. H. C. R.

Estimation and Separation of Rare Earth Metals from other Metals. I. Application of Hydrolysis to the Separation of Titanium, Iron, and Aluminium. LUDWIG MOSER and ERNST IRÁNYI (*Monatsh.*, 1923, 43, 673—677).—Titanium and aluminium may be separated by a method based on the differential hydrolytic dissociation of their salts. At a hydrion concentration of 0·05*N*, titanic salts are completely hydrolysed to give insoluble, non-colloidal, and therefore non-adsorbing, titanic oxide, whilst no hydrolysis of aluminium salts takes place. After fusion with alkali, the mixture is dissolved in dilute hydrochloric acid, the solution neutralised with sodium hydroxide (indicator methyl-orange), treated with 20 c.c. of hydrochloric acid (1 vol. concentrated acid : 9 vols. water), and allowed to become clear. Potassium sulphate (1 g.) and bromate (1·5 g.) are added, the solution diluted to 200 c.c., and boiled for half an hour, when quantitative separation of titanic oxide occurs (cf. *J.S.C.I.*, 1923, June). E. E. T.

Estimation and Separation of Rare Earth Metals from Other Metals. II. Separation of Titanium from Iron and Aluminium by Means of Sulphosalicylic Acid. LUDWIG MOSER and ERNST IRÁNYI (*Monatsh.*, 1923, 43, 679—684).—An aqueous solution of 4-sulphosalicylic acid, $SO_3H{\cdot}C_6H_3(CO_2H){\cdot}OH$, is prepared by diluting (etc.) the mixture obtained by heating salicylic acid with sulphuric acid. For the separation of titanium and iron, the mixture of oxides is fused with potassium hydrogen sulphate or sodium carbonate, and a solution made in dilute sulphuric acid. Sulphosalicylic acid solution is added, then ammonium carbonate until the colour changes from violet to red, and the iron precipitated by means of hydrogen sulphide.

Titanium and aluminium are separated as follows. The acid solution containing the two metals, after treating with sulphosalicylic acid, is strongly basified with ammonium carbonate, and then boiled for five minutes, when the titanium is precipitated as hydroxide.

The separation of the three metals concerned is effected as follows: (1) The mixture of oxides is weighed; (2) fused with alkali, dissolved in sulphuric acid, sulphosalicylic acid and then sufficient ammonium carbonate to give a red solution are added; the iron is precipitated as sulphide; (3) the filtrate from the ferrous sulphide saturated with ammonia, boiled, and the precipitated titanic hydroxide collected; (4) the aluminium is either estimated by difference, or the filtrate from (3) is evaporated, heated at 280° to remove sulphosalicylic acid, and the aluminium then estimated in the usual manner. E. E. T.

Estimation of Antimony by Means of Phenylthiohydantoic Acid. A. LASSIEUR and (MME) A. LASSIEUR (*Compt. rend.*, 1923, 176, 1221—1223).—Phenylthiohydantoic acid,

$$CO_2H{\cdot}CHPh{\cdot}NH{\cdot}CS{\cdot}NH_2,$$

prepared by boiling 95 parts of monochloroacetic acid with 75 parts of ammonium thiocyanate, 83 parts of aniline, and 450 parts of alcohol, is recommended as a precipitant for antimony. The

estimation of the metal is carried out as follows. The neutral solution diluted to 150 c.c. is acidified with 5 c.c. of *N*-acetic acid, and boiled with 0·5 g. of the reagent for five to six minutes. The precipitate is collected on a Gooch crucible and washed with water. For an approximate estimation, it can then be weighed as such after drying over sulphuric acid in a vacuum, calculating on the basis of an antimony content of 18·6%, but when accurate results are required the washed precipitate is dissolved in warm alcohol, and the antimony precipitated as sulphide by the addition of acetic acid and sodium sulphide. The precipitate is collected, washed, and dissolved in sodium sulphide solution, and the antimony is deposited electrolytically from the solution after the addition of 5 g. of potassium cyanide, and weighed. G. F. M.

The Detection of Traces of Stibine. EDWARD J. WEEKS (*Chem. News*, 1923, **126**, 275).—The gas to be tested is passed through a tube the walls of which are wetted with silver nitrate solution. A brown stain indicates the presence of stibine. A. R. P.

Detection of Bismuth in Urine. III. DOMENICO GANASSINI (*Boll. Chim. Farm.*, 1923, **62**, 193—195; cf. this vol., ii, 93).—The author replies further to Dezani's criticisms. As regards Dezani's method, according to which a yellow coloration is obtained when potassium iodide is added to a very dilute solution of a bismuth salt in presence of hydrochloric acid, the author suggests that the yellow liquid be shaken with its own volume of chloroform or carbon disulphide. Three cases may then present themselves: (1) If the yellow liquid becomes decolorised and the organic solvent assumes an amethyst colour, the presence of bismuth is excluded, the yellow coloration being due to free iodine. (2) If the yellow coloration is only partly lost, and the organic solvent acquires an amethyst tint, the presence of both bismuth and iodine is demonstrated. (3) If the yellow liquid retains its colour and the solvent remains colourless, bismuth is present. T. H. P.

A New Reaction for Rhodium and a Colorimetric Method for its Estimation. VASILI NIKOLAEVITSCH IVANOV (*J. Russ. Phys. Chem. Soc.*, 1917—1918, **49**, 601—603; **50**, 460—462).—Aqueous solutions of rhodium salts give, when mixed with stannous chloride, heated to boiling, and cooled, brown, colloidal solutions of the metal (analogous to those obtained with gold and platinum salts in the cold) which develop a fine crimson colour, doubtless owing to the gradual solution of the colloidal particles in the acid medium; the greater the amount of rhodium present the longer the colour takes to develop. In practice, the material examined is fused with potassium hydrogen sulphate, the fused mass lixiviated with a little water, and the filtered solution evaporated down to 1 c.c. To this an equal volume of a 40% solution of stannous chloride in 30% hydrochloric acid is added, the mixture heated to boiling and allowed to cool; rhodium is absent if a crimson colour does not develop in a few hours. For the quantitative estimation of the metal, the tint obtained is compared with that

of test solutions made up in the same way. The reaction will detect rhodium in a solution containing 0·0005 g. per litre.

G. A. R. K.

Detection of Benzene in Corpses. ALEXANDER O. GETTLER (*J. Pharm. Expt. Ther.*, 1923, **21**, 161—164).—The ground tissue is acidified with a few drops of sulphuric acid, steam-distilled, and the benzene extracted from the distillate with carbon tetrachloride. Addition of a 2 : 1 mixture of fuming nitric–sulphuric acids, with shaking, to the carbon tetrachloride solution converts the benzene into a mixture of the dinitrobenzenes, which are extracted with ether after evaporation of the solvent and neutralisation of the acid with sodium hydroxide. Qualitative tests for dinitrobenzene may then be applied. With suitable precautions, quantitative results may be obtained. E. S.

The Microchemical Estimation of Methyl along with Ethyl. WILLIAM KÜSTER and WILHELM MAAG (*Z. physiol. Chem.*, 1923, **127**, 190—195).—The mixture of methyl and ethyl iodides is absorbed in an alcoholic solution of trimethylamine, when the sparingly soluble tetramethylammonium iodide crystallises out, and can thus be separated from the soluble trimethylethylammonium iodide. Accurate results are obtained with from 10 to 20 mg. of substance. W. O. K.

Estimation of Dextrose in Sugar Mixtures. G. BRUHNS (*Chem. Ztg.*, 1923, **47**, 333—335).—The method of Willstätter and Schudel (A., 1918, ii, 337), which depends on the oxidation of dextrose by potassium iodide and sodium hydroxide to gluconic acid, was tested on solutions of pure dextrose, sucrose, and lævulose, on invert-sugar, and on solutions containing dextrin. It was found that sucrose was oxidised so as to give an apparent content of about 1·2% of invert-sugar with quantities of 1—4 g., whilst if only 0·1 g. of sucrose was taken an apparent content of 2·4% of invert-sugar was obtained. Pure lævulose is also attacked, and gave an apparent dextrose content of 9·8%. Invert-sugar, in consequence, appeared to contain more than 1% too much dextrose. By reducing the volume of sodium hydroxide added from 14·5 c.c. to 11 c.c., the apparent excess of dextrose was reduced to 0·55%. The method can therefore not be considered accurate for the estimation of dextrose in the presence of other sugars. H. C. R.

The Ferricyanide Method for Estimation of Blood-sugar. II. H. C. HAGEDORN and B. NORMAN JENSEN (*Biochem. Z.*, 1923, **137**, 92—95).—Using the authors' micro-method, errors of sampling are less than 0·5%. The presence of acetone or β-hydroxybutyric acid in blood does not introduce an error in the dextrose estimation, but uric acid and creatinine produce an error through reduction of the ferricyanide, equal approximately to one-half of their weight expressed as dextrose. H. K.

Estimation of Dextrose and Lactose in Blood and Urine. WM. THALHIMER and MARGARET C. PERRY (*J. Amer. Med. Assoc.*, 1922, **79**, 1506—1508).—The total sugar is first estimated as dextrose

by Folin and Wu's method for blood or serous fluids, or by Folin and Berglund's method for urine. The solution (which should be adjusted to contain about 0·3% of sugar) is then heavily inoculated with *Bacillus paratyphosus B*, and after incubation for forty-eight hours the sugar remaining is estimated as lactose.

CHEMICAL ABSTRACTS.

Estimation of Yeast Glycogen and the Action of Alkali on Glycogen-formation in Yeast. PAUL MAYER (*Biochem. Z.*, 1923, **136**, 487—497).—Glycogen can only be estimated in yeast when separated from yeast gum. The following method is recommended. Ten g. of yeast (pressed) were heated for three hours with 30 c.c. of 60% potassium hydroxide at 100°, cooled, and treated with 50 c.c. of water and 200 c.c. of 96% alcohol. After a day, the precipitated glycogen was filtered, washed twice with 60% alcohol, twice with absolute alcohol and ether, and the powder dissolved in hot water, filtered, neutralised with hydrochloric acid, and exactly saturated with ammonium sulphate. After ten hours, the glycogen is filtered, dissolved in hot water, and an aliquot portion hydrolysed with hydrochloric acid (2·2%) at 100°. The cooled solution is neutralised and the dextrose estimated by the Pavy-Kumagawa-Suto process. The results show that glycogen estimation in presence of yeast gum are too high, the actual values found for various races lying between 2·5 and 5·7% on the pressed yeast. Contrary to the findings of Elias and Weiss (A., 1922, i, 485), alkali does not stimulate yeast to form increased glycogen.

H. K.

Improved Volumetric Method for Estimating α-, β-, and γ-Cellulose. M. W. BRAY and T. M. ANDREWS (*Ind. Eng. Chem.*, 1923, **15**, 377—378).—The method depends on the oxidation of cellulose with potassium dichromate in sulphuric acid solution. Ten c.c. of a solution of the cellulose in 72% sulphuric acid are treated with 10 c.c. of potassium dichromate solution (90 g. per l.) and 60 c.c. of 72% sulphuric acid are added. The mixture is boiled for exactly five minutes, cooled on ice, and the excess of dichromate titrated with ferrous ammonium sulphate solution, using potassium ferricyanide as indicator. The dichromate solution is standardised in this way against 1 g. of cellulose obtained by the chlorination method of Cross and Bevan from sulphite pulp. For the estimation of α-, β- and γ-cellulose, 1 g. of the sample is triturated with 25 c.c. of the mercerising liquid (17·5% sodium hydroxide solution) and left for thirty minutes. The insoluble (α) cellulose is dried by suction on a filter pump, washed with 4% sodium hydroxide and distilled water, dissolved in 72% sulphuric acid, and estimated with dichromate as above. In one half of the filtrate, the β-+γ-cellulose is determined in the same way. In the other half, the β-cellulose is precipitated by carefully adding 10% sulphuric acid solution until neutral to methyl-orange, and then adding 5 c.c. of acid in excess. The precipitate is allowed to coagulate and the γ-cellulose estimated in the supernatant liquid as above. The β-cellulose is obtained by difference. The method is more accurate

and rapid than the gravimetric method and difficulties of filtration and washing are practically overcome. Check determinations can be made without repeating the Cross and Bevan chlorination, as is necessary in the gravimetric method. H. C. R.

Estimation of Formaldehyde in the Presence of Copper Sulphate. M. JAKEŠ (*Chem. Ztg.*, 1923, **47**, 386).—The usual methods of estimating formaldehyde cannot be applied directly to insecticide solutions containing copper sulphate. The copper is best removed by precipitation with potassium ferrocyanide. If the correct quantity of the latter is added, the solution will be found free from both copper- and ferrocyanide-ions after titration, as the excess of potassium ferrocyanide is removed by the formation of an insoluble potassium copper ferrocyanide. Before proceeding with the estimation of formaldehyde, the solution should be tested for the absence of both copper- and ferrocyanide-ions. The formaldehyde may then be oxidised with hydrogen peroxide, and the acid produced titrated with alkali, using azolitmin as indicator. If the excess of peroxide is boiled off, phenolphthalein may be used as indicator. H. C. R.

The Detection and Behaviour of Formaldehyde in Corpses. A. BRÜNING (*Ber. Deut. pharm. Ges.*, 1923, **33**, 99—103).—Owing to the rapidity with which formaldehyde is oxidised in the tissues, it can rarely be detected with certainty if any great length of time has elapsed before the toxicological examination, and the investigation should therefore be extended to include tests for the presence of formic acid. In the case of a body which had been some time in the water, a steam distillation of the liver with phosphoric acid revealed traces of formaldehyde by Hasse's peptone and sulphuric acid test in the first few drops of the distillate, but a negative test was given by all the other organs. The investigation of the same organs for formic acid, however, by Fincke's method gave a distillate which immediately reduced mercuric chloride, and after reduction with magnesium and hydrochloric acid with ice cooling, gave a strong formaldehyde reaction. The oxidation of formaldehyde by the oxydases in the tissues affords a possible explanation of the acid reaction of formaldehyde leather.
G. F. M.

New Reaction for Ketones. CAM. GILLET (*Bull. Soc. chim.*, 1923, [iv], **33**, 465—466).—Referring to the paper by Bougault and Gros (A., 1922, ii, 666) on the use of Nessler's reagent for the characterisation of ketones, the author directs attention to his prior publication on the same subject (*Bull Soc. chim. Belg.*, 1899, **13**, 170) and to that of Marsh and Struthers (P., 1908, **24**, 266).
G. F. M.

Use of Potassium or Sodium Bromide as a Source of Bromine for Urea Estimations. C. H. COLLINS (*Chem. News*, 1923, **126**, 180—181).—An apparatus is described for the preparation of small quantities of sodium hypobromite solutions for urea analyses. W. E. G.

Estimation of Urea in Blood by Folin and Wu's Method. A Modified Apparatus. GEO. G. BOGGS and W. S. McELLROY (*J. Lab. Clin. Med.*, 1923, 8, 254—255).—In the estimation of urea in blood by Folin and Wu's method, slight variations in pressure cause acid in the receiver to be drawn back into the receiving tube. The authors have modified the original apparatus in such a way that a slow current of air may be passed into the delivery tube so that a slight positive pressure is maintained and back suction prevented. The air current enters the delivery tube beyond the bend. It is found that no ammonia is lost even with a moderately fast current of air. CHEMICAL ABSTRACTS.

Estimation of Calcium Cyanamide. ALESSANDRO NANUSSO (*Giorn. Chim. Ind. Appl.*, 1923, 5, 168).—This method is based on the treatment of the silver salt of the cyanamide with ammonium chloride, and titration of the ammonia and guanidine thus formed with standard acid: $Ag_2N\cdot CN+2NH_4Cl=2AgCl+N:C\cdot N(NH_4)_2 \rightarrow NH_3+NH:C(NH_2)_2$ (cf. *J.S.C.I.*, 1923, June). T. H. P.

The Quantitative Millon's Reaction in Blood-serum, after Removal of the Proteins. I. GEORG HAAS (*Z. physiol. Chem.*, 1923, 127, 39—51).—The tyrosine content of the blood may be estimated colorimetrically, making use of Millon's reaction. Salts influence the development of the red colour. The quantity of tyrosine in the blood is increased in acute yellow atrophy of the liver. W. O. K.

The Colorimetric Reagent of Folin and Denis and Weiss's Modification of Millon's Test [Estimation of Tyrosine]. GEORG HAAS and WILLY TRAUTMANN (*Z. physiol. Chem.*, 1923, 127, 52—66).—If the tyrosine in the blood is estimated by the Folin-Denis phenol reagent, higher values are obtained than when estimated by Millon's reagent. The difference is no doubt due to the fact that the phenol reagent reacts with substances other than tyrosine. W. O. K.

A New Alkaloidal Reagent, and the Preparation of the Iodoantimonates of Alkaloids in Crystalline Form. CAILLE and E. VIEL (*Compt. rend.*, 1923, 176, 1156—1159).—An antimony reagent composed of antimonious oxide or chloride 5 g., hydrochloric acid (d 1·123) 20 c.c., potassium iodide 40 g., and water to 100 c.c., is a precipitant for organic amines, the solubility of the complexes formed increasing with decrease in molecular weight. In dilutions of 1 in 500 or less, only alkaloids are precipitated, and the sensitiveness of the reagent in this respect is of a high order, for example, 1 part of quinine in 100,000 parts being capable of detection by its means. The precipitates obtained are yellow, amorphous substances containing both antimony and iodine, the quinine compound, for instance, having the composition

$$C_{20}H_{24}O_2N_2SbI_3,2HI.$$

These iodoantimonites were also obtained in crystalline form by the method of François and Blanc (A., 1922, i, 851). G. F. M.

Estimation of Choline in Blood. JOHN SMITH SHARPE (*Bio. chem. J.*, 1923, **17**, 41—42).—The choline is extracted from the blood and tissues and is precipitated with iodine as the periodide. After washing off any free iodine, the periodide is decomposed with dilute nitric acid and the free iodine extracted with chloroform and titrated with standard sodium thiosulphate. The possibility of lecithin being formed as a degradation product is small if the estimation is carried out with reasonable speed. A recovery of 90—94% of choline added to blood was thus obtained. Normal blood to which no choline was added gave negative results. S. S. Z.

The Interconvertibility of Creatine and Creatinine. V. Estimation of Creatine in Muscle. AMANDUS HAHN and L. SCHÄFER (*Z. Biol.*, 1923, **78**, 155—160; cf. this vol., ii, 195).—The muscles are extracted with boiling 5% sodium chloride solution containing acetic acid and then with boiling water. Any proteins in the combined extracts are precipitated with trichloroacetic acid, which avoids adsorption of creatine and creatinine, and the creatine is then determined colorimetrically. Results are given for various muscles, which indicate that previous methods give rather low results. W. O. K.

Estimation of Morphine and of Secondary Alkaloids in Opium and its Galenical Preparations. MARIO AIAZZI MANCINI (*Boll. Chim. farm.*, 1923, **62**, 3—8, 35—39, 69—71, 101—105).—The author has investigated various methods for estimating morphine in opium, etc., including those given in the Pharmacopœias of the principal countries, and draws the conclusion that, as regards both accuracy and simplicity, the method of the U.S. Pharmacopœia is the most satisfactory. For the estimation of the secondary alkaloids, the methods of van der Wielen (A., 1903, ii, 519) and Tingle (A., 1918, ii, 87, 88, 175) are to be preferred. T. H. P.

The So-called Pyrrole Reaction. E. S. CHOTINSKI (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 149—153).—The pyrrole reaction, in which a pine shaving moistened with hydrochloric acid develops a red coloration on exposure to the vapours of pyrrole, is found also to be given by shavings of fir, cypress, linden, alder, birch, deal, pear, ash, and oak. Anderson (*Annalen*, 1858, **105**, 354) stated that this reaction is due to the presence of resin in pine shavings, and that an extract of the former in alcohol would also give the pyrrole reaction. This observation is repeated, and the extract found to give only a faint coloration, whilst the shaving, after extraction, gives as intense a coloration as before. The connexion between the pyrrole reaction and the coniferin reaction with phenols, whereby a blue coloration is produced, is shown, and the probability of the former reaction also being due to coniferin is pointed out. Coniferin is insoluble in alcohol, but soluble in hot water, and an aqueous extract of pine shavings gives a marked pyrrole reaction. Further, asparagus, which is rich in coniferin, but not resin, gives an intense red coloration with pyrrole vapours. R. T.

General and Physical Chemistry.

Use of Helium Light in Refractometry. N. Schoorl (*Ber.*, 1923, **56**, [*B*], 1047—1048).—Corrections are given which enable the helium lines (λ=6678, 5876, and 5016) to be employed with the Pulfrich refractometer, using only the tables supplied for the *D* line of sodium. The deviation of the emergent beam is measured in the usual way, and the corresponding refractive indices are obtained from the tables for the *D* line. The following corrections are then applied to give true refractive indices. The corrections are given in units of the fifth decimal place :

Line.	Prism Ic.	Prism IIc.
He red (λ 6678)	$-895/(n_D)$	$-1536/(n_D)$
He yellow (λ 5876)	$+23{\cdot}3/(n_D)$	$+41/(n_D)$
He green (λ 5016)	$+1582/(n_D)$	$+2775/(n_D)$

where n_D in each case denotes the apparent refractive index obtained from the tables.

The refractive index of the substance for the sodium line can then be calculated with sufficient accuracy by means of the formulæ : $n_D = n_{5876} - 0{\cdot}0255\,(n_{5876} - n_{6678})$ or $n_D = n_{5876} - 0{\cdot}0155(n_{5016} - n_{5876})$.

H. H.

The Theory of Band Spectra. H. A. Kramers and W. Pauli, jun. (*Z. Physik*, 1923, **14**, 351—367).—An explanation of band spectra is put forward based on the assumption that the electron impulse moment makes an angle with the line joining the atomic nuclei. The infra-red bands of diatomic molecules must be ascribed to radiation processes in which the atomic vibratory movements and the rotation of the molecule play a part. Only in the case of the halogen acids is the dispersion of the ultra-red bands so great that they can be resolved into discrete lines. The line missing in the middle of the bands corresponds with the rotationless condition, and the absence of this line is in agreement with the Bohr rule, that quantum conditions for which the impulse moment disappears possess no statistical weight. According to the Bohr theory, the rare gases and halogen-ions possess a resulting impulse moment $1 . h/2\pi$. If the same impulse moment be assumed for the halogen acids, then the distance between the innermost bands is three times as great instead of twice that of the distance between the other bands. This difficulty is overcome if the impulse moment makes an angle with the axis. An explanàtion is given of the negative group of oxygen bands described by Runge. The bands in the visible spectrum are due to strongly excited molecules in which the electron emitting light is directly influenced by the rotation of the molecule.

W. E. G.

The Mode of Excitation of the Atom and Molecule Spectrum by Electron Collisions. VICTOR VON KEUSSLER (*Z. Physik*, 1923, **14**, 19—31).—Experiments have been carried out on the intensities of the two hydrogen spectra in the absence and in the presence of helium at a pressure of hydrogen of 0·01 mm. Under a potential of 16 to 17 volts, the addition of helium did not cause any material change in the relative intensities of the two spectra. At slightly higher voltages, but still lower than the resonance potential of helium, the Balmer series became relatively more intense with respect to the secondary spectrum. In the presence of much helium, only the Balmer series is observed. Concurrently, the intensities of the individual lines of the Balmer series undergo change; in the presence of helium, the lines of short wave-length become more intense. These results and those of previous workers are explained on the assumption that the excited hydrogen molecules which normally emit the secondary spectrum, on collision with helium atoms, undergo dissociation into a normal and an excited atom with the subsequent emission of the Balmer series. Thus the dissociation of hydrogen occurs in two steps. The first is the excitation of the molecule by electron collision, and the second occurs when the excited molecule is subjected to atomic collisions before the emission of the radiation. The smallest ionisation step for hydrogen is the conversion of the H_2 molecule into a normal atom, a H^+ atom, and an electron. W. E. G.

The Effect of a Probable Electric Field on the Bands of Nitrogen. SNEHAMOY DATTA (*Astrophys. J.*, 1923, **57**, 114—120).—When the partial pressure of bromine vapour in a discharge tube containing air is gradually raised, the sharp bands of nitrogen become blurred until even the heads have disappeared. It is suggested that the blurring may be a Stark effect produced by the electric fields of the ionised bromine atoms, as predicted by Hettner. The similar blurring due to increased pressure in pure nitrogen may also be a Stark effect. The cyanogen band was unaffected by the bromine. The displacement observations recorded by Dufour (A., 1907, ii, 920) and by Clinkscales (*Physical Rev.*, 1910, **30**, 594) may also be a Stark effect. A. A. E.

Spectra Associated with Carbon. T. R. MERTON and R. C. JOHNSON (*Proc. Roy. Soc.*, 1923, [*A*], **103**, 383—395).—The authors have investigated the effect of the presence of helium in vacuum discharge tubes on the band and line spectra of carbon, and the conditions under which the different spectra can best be experimentally isolated. The Swan spectrum can be excited by means of uncondensed discharges in tubes with carbon electrodes and containing hydrogen, and provided with side tubes containing potassium hydroxide and phosphoric oxide. The Ångström bands appear in vacuum tubes containing carbon and oxygen when excited by uncondensed discharges and are usually accompanied by faint bands in addition to well-marked bands which are degraded to the violet. The faint bands, for the production of which hydrogen is essential, do not form part of the Ångström system, and can be

isolated as separate bands under appropriate conditions. The CH bands are observed with great brilliance in tubes provided with carbon electrodes and side tubes as described, and with a palladium regulator through which hydrogen is admitted. The high-pressure carbon monoxide bands may be isolated almost completely by employing a discharge tube containing carbon dioxide and provided with carbon electrodes and side tubes and palladium hydrogen regulator. On passing the discharge, the high-pressure bands appear after the carbon dioxide is reduced to carbon monoxide by the electrodes. "Comet-tail" bands may be isolated almost completely, the spectrum being accompanied only by a few feeble lines representing the principal lines of the helium spectrum, by employing a discharge tube provided with a palladium regulator, side tubes containing phosphoric oxide and potassium hydroxide, and containing helium at about 20 mm. pressure. The "comet-tail" bands appear suddenly after the tube has been run sufficiently long for all traces of water vapour and carbon dioxide to be absorbed and the quantity of hydrogen to be reduced very considerably. Particulars are given of the various lines observed. The measurements of wave-lengths and intensities are not in good agreement with those of Fowler (*Mon. Not. Roy. Astr. Soc.*, 1910, **70**, 484). When a small quantity of hydrogen is admitted to a vacuum tube exhibiting the comet-tail bands, these disappear almost completely, and are replaced by a spectrum consisting of well-marked triplet-bands degraded to the red, with some indication of Swan and Ångström bands. Details are given of a new spectrum of carbon excited when a condensed discharge is passed through a wide-bore tube with carbon electrodes containing helium at a pressure of about 20 mm., and such that an uncondensed discharge would excite the "comet-tail" spectrum. It is suggested that the function of helium in the discharge tubes under the conditions of the experiment is to permit the passage of a discharge, thus enabling spectra appropriate to extremely low pressures of other gases present in the tube to be excited. J. S. G. T.

The Series Spectrum of Trebly-ionised Silicon (Si^{IV}). A. Fowler (*Proc. Roy. Soc.*, 1923, [*A*], **103**, 413—429).—Numerous new lines of silicon have been observed and have been classified in four groups, in extension of the groupings made by Lockyer in connexion with stellar spectra. The four groups represent successive stages of ionisation, and are designated Si^{I}, Si^{II}, Si^{III}, and Si^{IV}. The spectra consist alternately of triplets and doublets, and the series constant has successive values N, $4N$, $9N$, and $16N$, where N is the series constant for hydrogen. The value $16N$ for the series constant of Si^{IV} is fully established by the new data. The spectrum resembles that of neutral sodium Na^{I}, but the main series corresponding with the familiar series of Na^{I} are in the extreme ultra-violet. The secondary series which fall partly within the ordinary range of observation, correspond with series occurring in the infra-red in the case of Na^{I}. A comparison of the series spectra of the elements Si^{IV}, Al^{III}, Mg^{II}, and Na^{I}, the atoms of

which are characterised by the same number and distribution of external electrons whilst the nuclei differ in charge and mass, indicates that differences in the four spectra are to be attributed mainly to differences in the nuclear charges, or to differences in the net charges of the atoms as a whole with respect to the electron producing the spectrum by its transitions from one quantum orbit to another. The respective doublet separations in the respective series are as follows: Na^{I}, 17·18; Mg^{II}, 91·55; Al^{III}, 238; Si^{IV}, 460. These and the series terms exhibit greater regularity than those for elements of the same chemical group. The largest term in the Si^{IV} series system corresponds with the $1(\sigma)$ or 3σ(Bohr) term and is equal to 364,117, corresponding with a value of the ionisation potential equal to 44·95 volts. J. S. G. T.

Regularities in the Band Spectrum of Silicon. C. PORLEZZA (*Gazzetta*, 1923, **53**, i, 215—224; cf. this vol., ii, 198).—The bands observed by the author in the arc spectrum of silicon and also those obtained by de Gramont and Watteville (A., 1908, ii, 909) by burning silicon chloride or by passing a spark between silicon electrodes may be grouped into the five series: (1) $1/\lambda=37812+1185{\cdot}5m+6{\cdot}25m^2(m=0, 1, 2, 3, 4)$; (2) $1/\lambda=36288+1170{\cdot}6m+5{\cdot}2m^2(m=0, 1, 2, 5, 6)$; (3) $1/\lambda=35966+1152{\cdot}2m+5{\cdot}95m^2(m=0, 1, 4, 5, 6, 7)$; (4) $1/\lambda=35632+1139m+6{\cdot}2m^2(m=0, 4)$; (5) $1/\lambda=38738+1170{\cdot}8m+4{\cdot}4m^2(m=0)$. As regards the grouping in series, it is shown that, just as for the line spectra, the arc spectrum of silicon is intermediate to the flame and spark spectra, as regards both the number and the intensity of the bands. T. H. P.

The Explosion Spectra of the Alkaline-earth Metals. R. A. SAWYER and A. L. BECKER (*Astrophys. J.*, 1923, **57**, 98—113; cf. A., 1922, ii, 242, 803; Anderson, *Astrophys. J.*, 1920, **51**, 37).—The explosion spectra of the chlorides of barium, calcium, magnesium, and strontium between λ 2280 and λ 4550 have been investigated, using the asbestos fibre method, and found, in agreement with the theoretical conclusions of Saha and of Sommerfeld, to be almost pure spark spectra, consisting chiefly of the doublets of the first and second subordinate series, $2p-md$ and $2p-ms$. Only the fundamental singlet arc line $1S-2P$ appears, with a relative intensity corresponding with that in the spectra of the solar chromosphere and class B stars. So small an amount of material is required to give explosion spectra that lines due to copper, zinc, aluminium, lead, carbon, and nitrogen present as impurities were prominent; lines of chlorine, hydrogen, and oxygen were not detected. A. A. E.

Röntgen Ray Spectroscopic Measurements. Röntgen Ray Spectra. ELIS HJALMAR (*Z. Physik*, 1923, **15**, 65—109).—Particulars are given of the determination of the *M*-series of lines in the *X*-ray spectra of uranium, thorium, bismuth, lead, thallium, gold, platinum, iridium, osmium, tungsten, tantalum, lutecium, ytterbium, erbium, holmium, and dysprosium, and of the *N*-series

of lines of uranium, thorium, and bismuth. In the case of the *M*-series, the complexity of the strong lines is established. Certain new lines are recorded and arranged in the general classification of *X*-ray spectra. The validity of the combination principle in the case of these lines is established. Certain *N*, *O*, and *P* levels can be calculated from them, and the values agree with those determined by Coster and Bohr. The results in the case of the *N*-series are in agreement with previous results.

The existence of differences in the calculated values of the wave-length of a line when determined by the application of Bragg's formula $n\lambda = 2d \sin \phi$ to spectra of different orders is definitely established. The experimental results in this connexion are critically examined, and it is shown that the reflection theory of the production of the lines due to Ewald (*Ann. Physik*, 1917, [iv], **54**, 519), leading to the relation $\log (\sin \phi/n) = \text{const.} + A/n^2$, where A is a constant, is alone compatible with the determinations, and affords results according in some measure with the deviations from a constant value observed in the various orders of spectra.

J. S. G. T.

The Arc Spectrum of Celtium. JACQUES BARDET (*Compt. rend.*, 1923, **176**, 1711—1712).—A complete list is given of the wave-lengths of the lines of the arc spectrum of celtium, the material employed for the research being zirconium containing besides celtium only a trace of lead. The measurements were made over the region comprised between 2300 and 3500 Å. G. F. M.

The *L*-Series of Hafnium. AUGUST ŽÁČEK (*Z. Physik*, 1923, 15, 31—32).—A hafnium preparation, a mixture of hafnium and zirconium oxides, has been used for the measurement of the *L*-series. The stronger lines have been measured by the absolute method. The values of λ were α_1, 1566,14; α_2, 1576,70; β_1, 1370,17; β_2, 1323,6; β_3, 1349,1. W. E. G.

Absorption in Iodine and Other Vapours. K. VOGT and J. KOENIGSBERGER (*Z. Physik*, 1923, **13**, 292—311).—The selective absorption, absorption bands, and lines of iodine vapour, of bromine and nitrogen peroxide vapours, have been measured over a range of temperatures, pressures, and thicknesses. The selective absorption of iodine broadens with increase in temperature, the maximum retaining its position unchanged, but the amount of absorption being smaller at the higher temperatures. The selective and band absorption become fainter above 600°, giving rise to a typical line spectrum. The selective and band absorption are to be ascribed to the molecule or to some condition peculiar to molecule formation. Beer's law holds for iodine only up to thicknesses, $5 \cdot 10^{-5}$. Experiments with bromine confirmed the limits of applicability of this law given by Ribaud. Addition of air increased the absorption slightly on the short wave-length side and to a considerable extent on the long wave-length side of the maximum. Calculation of the selective absorption and comparison with the experimental

values have been made, and better agreement is obtained on the short wave-length side than on the long wave-length side of the maximum. The number of molecules taking part in the continuous absorption at any moment is 1/100 of the total present. The band spectrum of iodine at low densities possesses a channelled appearance, which disappears on raising the density. At high densities, the single absorption lines of bromine became broadened, as did also a number of iodine, bromine, and nitrogen peroxide lines when the density was increased by the addition of foreign gases. The cause of this widening is traced to the molecular collisions. The rotation Doppler-effect does not occur to an appreciable extent.

W. E. G.

The Absorption of Near Ultra-red Radiation by Carbon Dioxide. JUNZÔ ÔKUBO (*Sci. Rep. Tôhoku Imp. Univ.*, 1923, **12**, 39—43).—It is shown that in agreement with the results of Hertz (A., 1911, ii, 830) and of Bahr (A., 1913, ii, 6) the near ultra-red absorption spectrum of gaseous carbon dioxide comprises intense bands at $\lambda\lambda$ 2·71 and 2·77 μ and a somewhat weaker band at λ 2·61 μ. In addition, feebler maxima occur at $\lambda\lambda$ 3·02, 2·99, 2·97, 2·93, 2·88, 2·84, 2·81, 2·73, 2·67, 2·63, 2·57, 2·53, 2·48, 2·44, 2·40, 2·37, 2·34, and 2·29 μ. These weaker maxima are not so prominent as in the case of the spectra of diatomic molecules, *e.g.*, hydrochloric acid.

J. S. G. T.

The Ultra-violet Absorption Spectra of Eugenol and *iso*-Eugenol. GARTHA THOMPSON (T., 1923, **123**, 1594—1597).

Absorption Spectra of Sulphuric and Nitrated Solutions of Phenanthroxazine and Phenanthrazine. B. FORESTI and R. MARTORELLI (*Gazzetta*, 1923, **53**, i, 262—264).—Examination of the absorption spectra of sulphuric acid solutions, with and without addition of a nitrate, of phenanthroxazine and phenanthrazine and of a mixture of 77·4 parts of the former with 22·6 parts of the latter, confirms the results previously obtained (A., 1922, i, 1062; ii, 524). Sulphuric acid solutions of phenanthroxazine exhibit an absorption band at about 500 $\mu\mu$ and an absorption decreasing continuously from the extreme red to about 560 $\mu\mu$; when nitrate is present, an intense absorption band is shown at about 575 $\mu\mu$ and a slight absorption in the violet. With phenanthrazine, a sharp absorption band occurs at about 620 $\mu\mu$ and a moderate absorption in the extreme violet; when nitrate is present, the absorption begins at about 600 $\mu\mu$ and increases rapidly towards the violet, culminating in a band at about 470 $\mu\mu$. Absorption curves deduced from photographs of the spectra are given.

T. H. P.

The Ultra-violet Absorption Spectra of Alkaloids of the *iso*Quinoline Group. Narceine. PIERRE STEINER (*Compt. rend.*, 1923, **176**, 1379—1381; cf. Hartley, A., 1885, 1174; Dobbie and Lauder, T., 1903, **83**, 605).—The study of the ultra-violet absorption spectrum by Henri's method shows a large band the maximum

of which lies at $\lambda=2707$ Å. with a maximum absorption coefficient of $\epsilon=9800$, the minimum values being $\lambda=2539$ Å. and $\epsilon=8000$. A diagram is given which shows the spectrum of narceine in comparison with those of narcotine, opianic acid, and hydrocotarnine; certain similarities in the curves are pointed out. It is stated that a spectrographic estimation of 0·05 mg. of narceine in 2 c.c. of solvent may be effected. H. J. E.

Phosphorescence caused by Active Nitrogen. W. JEVONS (*Nature*, 1923, **111**, 705—706; cf. Lewis, this vol., ii, 361).—In the course of an observation of the spectrum resulting from the introduction of aluminium chloride vapour into a stream of active nitrogen, it was noticed that after long exposure a solid deposit was produced which exhibited a bright green fluorescence when brought into contact with active nitrogen some days later. A. A. E.

Photochemical Studies. XVI. The Inapplicability of the Photoelectric Law to Photochemical Reactions. J. PLOTNIKOW (*Z. wiss. Photochem.*, 1923, **22**, 110—116).—From a review of recent work on the subject, the author concludes that Einstein's photoelectric law expressed by the equation $mv^2/2=h\nu$, in which the symbols have the customary significance, is inapplicable to photochemical reactions (cf. A., 1922, ii, 248). J. S. G. T.

The Photochemical Decomposition of Solid Substances. ALBERT NOYES, jun. (*Compt. rend.*, 1923, **176**, 1468—1470).—A theoretical paper in which Perrin's radiation theory (A., 1919, ii, 177) is developed in the sense of a slight modification in dealing with solid substances. This modification is necessary as a certain amount of energy is required to separate the molecules and also to remove the products of the decomposition from the surface. The reaction velocity for a given frequency is represented by $dx/dt=kI(h\nu-h\nu_0)$, where I is the intensity of the light and $h\nu_0$ the energy used in separating the molecules from each other. If energy of several frequencies is used, the equation becomes $dx/dt=kI[(h\nu_1-h\nu_0)+(h\nu_2-h\nu_0)+\ .\ .\ .\ +(h\nu_n-h\nu_0)]$. H. J. E.

Inhibition of the Photochemical Decomposition of Hydrogen Peroxide Solutions. II. WILLIAM THEODORE ANDERSON, jun., and HUGH STOTT TAYLOR (*J. Amer. Chem. Soc.*, 1923, **45**, 1210—1217; cf. this vol., ii, 278).—Using the method previously described, the authors have investigated the decomposition of hydrogen peroxide by ultra-violet light in the presence of a number of inorganic acids, bases, and salts as inhibitors of the decomposition. The inhibition constant is given for perchloric, nitric, sulphuric, phosphoric, boric, and hydrochloric acids, sodium, potassium, ammonium, barium, ethylammonium, and phenylammonium hydroxides, sodium, potassium, ammonium, and magnesium sulphates, sodium and barium nitrates, potassium perchlorate, sodium fluoride and chloride, ammonium chloride and bromide, potassium chloride and bromide, and barium bromide. With the exception

of the nitrates, which show a weak absorption of light throughout the ultra-violet, the substances are practically diactinic to the incident radiation. The bases are found to be excellent inhibitors, the acids good inhibitors, and the bromides and chlorides moderately strong inhibitors, whilst all other inorganic compounds examined were found to be without action. The inhibition was shown by neutral salt action to be a function of the concentration of the hydrogen-, chloride-, bromide-, and hydroxyl-ions. A tentative hypothesis of the mechanism of the action has been put forward which is based on an ionisation of the hydrogen peroxide, and the facts, which must be covered by any hypothesis of the action, have been enumerated. J. F. S.

Reduction of Carbon Dioxide by Ultra-violet Light. H. A. Spoehr (*J. Amer. Chem. Soc.*, 1923, **45**, 1184—1187).—The author discusses briefly the work of Usher and Priestley (A., 1911, ii, 817), Stoklasa and Zdobnický (A., 1911, i, 178, 769), Berthelot and Gaudechon (A., 1910, i, 543), and Baly, Heilbron, and Barker (T., 1921, **119**, 1025) on the action of ultra-violet light on carbon dioxide. The experiments have in many cases been repeated, but in no case has the production of formaldehyde been confirmed. Paracetaldehyde itself is shown to break up readily under the action of ultra-violet light, forming acetaldehyde and probably glycollaldehyde, which at 60° readily passes into a hexose. Thus paracetaldehyde, far from being a protection against sugar formation, itself, quite independently of the presence of carbon dioxide, yields substances which reduce alkaline copper solutions. The author feels that in the publications named some essential condition or factor has been omitted in the description, or, failing this, a misinterpretation of experimental observations has occurred. J. F. S.

Photochemistry of Potassium Permanganate. II. Energetics of the Photo-decomposition of Potassium Permanganate. E. K. Rideal and R. G. W. Norrish (*Proc. Roy. Soc.*, 1923, [*A*], **103**, 366—382).—In continuation of previous work (this vol., ii, 362), the authors have investigated the absorption spectrum of a $0\cdot01N$-solution of potassium permanganate, more especially in the ultra-violet, in order to determine the wave-length of the light effecting the decomposition of potassium permanganate, and to test the validity of Einstein's photochemical law in this connexion. In the absorption spectrum, a band occurred between $\lambda\lambda$ 380 and 270 $\mu\mu$, with its head at λ 313 $\mu\mu$, whilst beyond λ 260 $\mu\mu$ a second band commenced. The visible radiations of the mercury-vapour spectrum were not appreciably effective in decomposing potassium permanganate, and it is considered that the line at λ 3128 Å. is principally responsible for the photo-decomposition by mercury-vapour light. Assuming that the only photo-active line is at λ 3128 Å. and that the coefficient of absorption for green and yellow light is the same as for the ultra-violet light, it is shown that two quanta are probably concerned in the photo-

decomposition of the permanganate-ion. It was found that mixtures of potassium permanganate and oxalic acid were much more sensitive to ultra-violet light than to visible light. The mechanics of the photo-decomposition are discussed from the point of view of atomic structure suggested by Kossel, Lewis, and Langmuir.

J. S. G. T.

Action of Light on Double Tartrates. V. VOLMAR (*Compt. rend.*, 1923, **176**, 1465—1467; cf. this vol., ii, 279).—Solutions of potassium antimonyl tartrate and the corresponding compounds of arsenic, bismuth, copper, and iron undergo decomposition on exposure to ultra-violet light with liberation of the metal, the maximum effect being produced in the case of the bismuth compound. The simple salts of the same metals, both organic and inorganic, are quite stable under similar conditions. The conclusion is drawn that the heavy metal in the tartrates occupies a position in the molecule in accordance with the constitution attributed to it by Jungfleisch. Potassium borotartrate furnishes an exception; the author considers this to be due to the fact that it appears to be, not a definite compound, but a mixture.

H. J. E.

The Capture of Electrons by Swiftly Moving α-Particles. BERGEN DAVIS (*Nature*, 1923, **111**, 706).—The failure of an α-particle, when in the act of ionising a molecule, or immediately after, to attach one or more of the free electrons to itself may be due to the high velocity of the α-particle. When its velocity has fallen from $20{\cdot}6\times10^8$ cm./sec. to $8{\cdot}2\times10^8$ cm./sec. one electron is taken up, and at a velocity of $3{\cdot}1\times10^8$ cm./sec. the second electron is taken up. The limiting parabolic velocities for an electron falling into the *K*-ring of (*a*) a doubly charged α-particle, and (*b*) one having a single charge are calculated to be 6·2 and $3{\cdot}2\times10^8$ cm./sec., respectively. It is therefore suggested that if the α-particle is moving with a velocity greater than that of the fall of an electron into the *K*-ring, the electron will fail to reach the *K*-ring and effect a combination. In that case, all α-rays, of whatever initial velocity, should capture the first and second electrons at the same velocity.

A. A. E.

The Employment of Normal Radium and Uranium Solutions for Emanation Measurements. P. LUDEWIG and E. LORENSER (*Z. Physik*, 1923, **13**, 284—291).—The constancy and usefulness of normal solutions of radium and uranium as standards for the determination of radioactive material has been tested by comparison of the amounts of emanation liberated under comparable conditions from a number of radioactive solutions over wide intervals of time. A number of normal solutions of radium from the Physikalisch Technischen Reichsanstalt, analysed by measurements of the emanation, agreed within 1%, and a series of uranium solutions prepared in the Freiberg Radium Institute agreed within 0·5% with the Reichsanstalt solutions. The temperature at which the emanation is transferred to the ionisation chamber does not play

any part. The radium and uranium solutions showed no deterioration when tested over a period of twelve months. The accuracy of this method is about 1%. W. E. G.

Electrolytic Dissociation of Hydrogen Selenide and Hydrogen Telluride. DE HLASKO (*J. Chim. Phys.*, 1923, **20**, 167—172).—The electrical conductivity of sodium hydroselenide has been determined at 25° in an atmosphere of hydrogen and the following values of the molecular conductivity have been found, μ_{100} 112, μ_{500} 115, and μ_{1000} 118. From these values, the value of μ_{∞} is deduced as 120·5, and since at this temperature the sodium ion has the value $\lambda_{Na^{\cdot}}=50$, the value of $\lambda_{SeH'}$ is about 70. Using the same method and apparatus, the electrical conductivity of solutions of hydrogen selenide has been measured at 25° in an atmosphere of hydrogen. The following data are recorded: 0·1N $\mu=17·9$, $\kappa=1·79\times10^{-3}$, $\alpha=0·0424$, $K^{25°}_{H_2Se}=\alpha^2/(1-\alpha)v=1·88\times10^{-4}$; 0·0249$N$, $\mu=35·3$, $\kappa=8·80\times10^{-4}$, $\alpha=0·0836$, $K=1·90\times10^{-4}$; 0·0137N, $\mu=46·0$, $\kappa=6·54\times10^{-4}$, $\alpha=0·1091$, $K=1·88\times10^{-4}$; 0·00817N, $\mu=59·5$, $\kappa=4·86\times10^{-4}$, $\alpha=0·1410$, $K=1·86\times10^{-4}$, the mean value of the ionisation constant, K, being $1·88\times10^{-4}$. A similar series of measurements has been made for hydrogen telluride solutions at 18°. The following data are recorded: 0·093N, $\mu=56$, $\kappa=5·24\times10^{-3}$, $\alpha=0·148$, $K^{18°}_{H_2Te}=\alpha^2/(1-\alpha)v=2·40\times10^{-3}$; 0·0667$N$, $\mu=63$, $\kappa=4·215\times10^{-3}$, $\alpha=0·166$, $K=2·23\times10^{-3}$; 0·06173N, $\mu=66$, $\kappa=4·061\times10^{-3}$, $\alpha=0·174$, $K=2·26\times10^{-4}$; 0·06024N, $\mu=67$, $\kappa=4·061\times10^{-3}$, $\alpha=0·176$, $K=2·26\times10^{-3}$; 0·03442N, $\mu=85·5$, $\kappa=2·942\times10^{-3}$, $\alpha=0·225$, $K=2·22\times10^{-3}$; 0·02326N, $\mu=107·5$, $\kappa=2·497\times10^{-3}$, $\alpha=0·283$, $K=2·59\times10^{-3}$, 0·01186N, $\mu=136$, $\kappa=1·607\times10^{-3}$, $\alpha=0·360$, $K=2·50\times10^{-3}$, 0·00278N, $\mu=208·5$, $\kappa=5·79\times10^{-4}$, $\alpha=0·549$, $K=1·80\times10^{-3}$. The mean value of the dissociation constant is $2·27\times10^{-3}$. According to the present experiments, hydrogen telluride is a stronger acid than hydrogen fluoride. The increase in the strength of the hydrogen acids of the elements of group VI thus increases rapidly with increasing atomic weight, as is shown by the dissociation constants of these substances thus: H_2O, $K=0·64\times10^{-14}$, H_2S, $K=0·91\times10^{-7}$, H_2Se, $K=1·88\times10^{-4}$, H_2Te, $K=2·27\times10^{-3}$. J. F. S.

The Question of Unipolar Conductivity of Metallic Sulphides. The Investigation of the Electrical Properties of Silver Sulphide and Cuprous Sulphide. GEORGI GRIGORE-VITSCH URAZOV (*J. Russ. Phys. Chem. Soc.*, 1919, **51**, 311—352).—The conductivities of silver sulphide and cuprous sulphide were investigated at different temperatures, using an alternating current. The samples investigated were prepared synthetically taking great precautions to ensure their uniformity, etc. It is shown that the conductivity of these sulphides changes with temperature in accordance with the formula $\lambda_t=\lambda_0\times e^{\alpha t}$. The presence of excess of either metal or sulphur greatly increases the conductivity of the sulphides, particularly the presence of sulphur in cuprous sulphide. The transition points of the different modification of the sulphides

are clearly shown on the conductivity curves. Both sulphides are shown to decompose into their components under the influence of a direct current, as evidenced by the isolation of the components at the electrodes and the detection of a considerable back *E.M.F.*
G. A. R. K.

The Critical and Dissociation Potentials of Hydrogen. A. R. Olson and George Glockler (*Proc. Nat. Acad. Sci.*, 1923, 9, 122—126).—An apparatus is described for the measurement of the current voltage curves. The dissociation potential of hydrogen is found to be 3·16 volts. Values are obtained for the dissociation potentials of five members of the Lyman series. Breaks on the current voltage curves, corrected for the dissociation voltage, 3·16 volts are recorded at 11·98, 12·68, 12·98, 13·14, and 13·24 volts, and these are in good agreement for the calculated values of the Lyman series. In addition, three breaks occur at 14·86, 15·35, and 15·62 volts, which are ascribed to the hydrogen molecule.
W. E. G.

Luminous Discharge in Bromine. A Possible Determination of the Ionisation Potential of Bromine. W. Albert Noyes, jun. (*J. Amer. Chem. Soc.*, 1923, **45**, 1192—1195).—Using practically the same apparatus and method as was previously employed in the investigation of the luminous discharge in iodine (this vol., ii, 209), the ionisation potential of bromine is found to be $12·5\pm0·5$ volts. The fact that for tubes of a given length approximately the same multiple of the ionisation potential of bromine as of iodine was obtained is accounted for by the higher heat of dissociation of bromine, the molecules having little or no electron affinity. The higher electron affinity of bromine would thus be counterbalanced by a lower concentration of the monatomic gas. The facts agree with the work of Gibson and Noyes on the sparking potentials in gases (A., 1922, ii, 812). J. F. S.

The Ionising Potentials of Nitrogen and Hydrogen. H. D. Smyth (*Nature*, 1923, **111**, 810; cf. *Proc. Roy. Soc.*, 1922, [*A*], **102**, 283).—In the case of nitrogen, the three critical potentials, 16·9, $24·1\pm1·0$, and $27·7\pm1·0$ volts, are interpreted as corresponding respectively to the transitions $N_2 \longrightarrow N_2^+ + e^-$; $N_2 \longrightarrow N^{++} + N + 2e^-$; and $N_2 \longrightarrow 2N^+ + 2e^-$. If this is correct, the first ionising potential of atomic nitrogen is about 11 volts, and the second about 18 volts. The ionisation of molecular hydrogen in the neighbourhood of 16·5 volts does not appear usually to be accompanied by dissociation. A. A. E.

Collodion Membrane for Liquid Junctions. Harold A. Fales and Mortimer J. Stammelman (*J. Amer. Chem. Soc.*, 1923, **45**, 1271—1272).—With the object of preventing the mechanical intermixing of one liquid with another during the measurement of hydrogen-ion concentrations by the *E.M.F.* method, the authors have covered the ends of the electrode vessels with a film of collodion. The membrane is best produced by allowing some collodion to

evaporate in the air until it becomes thick and then dipping the end of the syphon tube of the electrode vessel into it, withdrawing, and allowing the collodion to dry. This process is repeated several times. The membrane may only be used when the collodion is equally permeable to all the ions in the solutions used. If this is not the case, large potential differences will be set up owing to the setting up of the "Donnan equilibria"; measurements given in the paper show that very constant *E.M.F.* measurements can be obtained with this device. J. F. S.

Calculation of Isoelectric Points. P. A. LEVENE and HENRY S. SIMMS (*J. Biol. Chem.*, 1923, **55**, 801—813).—On the assumption that the ionisation of each acidic and basic group in a poly-acidic, poly-basic amphoteric substance takes place independently of the degree of ionisation of other groups in the molecule, the following approximate formula has been deduced for the isoelectric point of the ampholyte: $I=\sqrt{(\Sigma Ka)/(\Sigma Kb) \, . \, K_W}$. The accurate expression is also given in the original. Since the values of the dissociation constants of the weaker acidic and basic groups are negligible in comparison with those of the strongest, the above formula may be simplified, without much error, to $I=\sqrt{Ka/Kb \, . \, K_W}$, in which K_a and K_b represent the dissociation constants of the strongest acidic and basic groups, respectively. The latter formula is identical with the one usually employed for the calculation of the isoelectric point of a monoacidic, monobasic ampholyte. Using the above expressions for the calculation of the isoelectric point of aspartic acid, the value $P_I=2{\cdot}76$ was obtained in each case. E. S.

Transport Numbers of Sodium and Potassium in Mixed Chloride Solution. R. F. SCHNEIDER and S. A. BRALEY (*J. Amer. Chem. Soc.*, 1923, **45**, 1121—1134).—The transport numbers of sodium and potassium and the transport ratio have been determined in mixtures of the chlorides of these metals in solutions varying in concentration from $0{\cdot}1N$ to $1{\cdot}6N$. The ratio of the molecular concentration of the two salts was varied from 3KCl : 1NaCl to 1KCl : 3NaCl. The equivalent conductivity of the mixtures have also been determined. The ionic conductivities have been calculated from the transport numbers and the equivalent conductivities of the different solutions examined. The results show that the solutions are highly complex and in no way in accord with the Ghosh hypothesis of complete dissociation. The mobility of the sodium-ion at a total concentration of $\cdot02N$ and a ratio of 3KCl : 1NaCl has been shown to be practically zero. The deviations between the calculated values and the experimental values of the transport ratios are not due to hydration of the ions alone, but must be due also to the formation of complexes in solution. The present results agree well with those of Smith and Ball (A., 1917, ii, 247) and Smith and Webb (A., 1920, ii, 361), in which they found that the sodium-ion fraction increases with increase in total concentration above $0{\cdot}2N$. Below this concentration, the sodium-ion fraction decreases with respect to that of the potassium-ion. See also

A., 1921, ii, 662. Various explanations of the behaviour observed are discussed. J. F. S.

Production of Sulphuric Acid and Sodium Hydroxide by Electrolysis of Sodium Sulphate. E. R. WATSON (*J. Soc. Chem. Ind.*, 1923, **42**, 251—252T).—By the electrolysis of 40% aqueous sodium sulphate solution, employing a platinum, iron, or copper cathode and a platinum, lead, or carbon anode, a current density of about 4 amperes per sq. dcm., and a potential difference between the electrodes of about 5 volts, starting the electrolysis at about 30° and allowing the temperature to rise to about 40°, conversion into sodium hydroxide and sulphuric acid can be effected with a current efficiency of about 90%, and an energy efficiency of about 50%, provided electrolysis is not carried beyond an average conversion of about 25%. Nearly all the sodium sulphate may be crystallised out of the alkaline liquor, leaving sodium hydroxide in the mother-liquor nearly pure, and sodium hydrogen sulphate may be similarly obtained from the acid liquor. Sulphuric acid is best produced from the sodium hydrogen sulphate by distillation. J. S. G. T.

Electrochemical Properties of Bismuth and Antimony in Alkaline Solution. G. GRUBE and F. SCHWEIGARDT (*Z. Elektrochem.*, 1923, **29**, 257—264).—The behaviour of bismuth and antimony employed as anode in solutions of sodium hydroxide and potassium hydroxide has been investigated. Both bismuth and antimony dissolve anodically in the form of tervalent ions in strong alkali solution. Thus, as much as 1 g. of bismuth may be dissolved in 1 litre of concentrated alkali hydroxide solution, with the formation of an alkali bismuthite. The anode then becomes passive and covered with coloured higher oxides of bismuth. In the case of antimony, concentrated solutions of potassium antimonite may be obtained in this manner without the anode being rendered passive. Passivity of the antimony anode results, however, if the current density exceeds 7·5 amperes per sq. dcm., and the anode then becomes covered with a white non-conducting layer of oxide. A solution of potassium antimonite is a strong reducing agent and readily absorbs oxygen from the air. The process of its electrolytic oxidation at a polished platinum electrode is not, however, reversible, and it is shown that production of potassium antimonate in this manner is effected, not by a direct process of anodic oxidation, but owing to the oxidising action of oxygen evolved in the form of gas at the electrode. The electrode potential, ϵ, of antimony in a $10N$-solution of potassium hydroxide at 20°, the process of solution being represented by $Sb+4OH'+3\oplus \rightarrow SbO_2'+2H_2O$, is given by $\epsilon=-0{\cdot}675+0{\cdot}058/3 \log c_{SbO_2'}$. For the oxidation process to antimonate, the corresponding equation is $SbO_2'+2OH'+2\oplus \rightarrow SbO_3'+H_2O$, and the value of ϵ is given by $\epsilon=-0{\cdot}589+0{\cdot}058 \log (c_{SbO_3'}/c_{SbO_2'})/2$. The value of the electrode potential of antimony in a solution containing 1 g. ion of SbO_3' in $10N$-potassium hydroxide solution is $-0{\cdot}641$ volt. The value of the antimonite–antimonate potential difference is reduced

as the alkalinity of the solution is increased, and is determined by the OH′ concentration of the solution. J. S. G. T.

Thermostats. A. TIAN (*J. Chim. Phys.*, 1923, **20**, 132—166).—A general discussion on the erection of thermostats. A method is described whereby a thermostat having several ranges may be constructed. J. F. S.

Critical Quantities. W. HERZ and EBERHARD NEUKIRCH (*Z. physikal. Chem.*, 1923, **104**, 433—450).—The authors record a number of determinations of critical temperature, density, and pressure. These include the following: chloroform, t_c=262·5±0·2°, d_c 0·496; diethyl amine, t_c 223·8±0·2°, d_c 0·243; triethylamide, t_c 262·2±0·2°, d_c 0·257; acetone, t_c 235·6±0·2°, d_c 0·252; methyl sulphide, t_c 229·0±0·2°, d_c 0·301; ethyl bromide, t_c 230·8±0·2°, d_c 0·507; *n*-butyl alcohol, p_c 48·4±0·5 atm.; pyridine p_c 60·0±0·5 atm., phenol, p_c 60·5±0·5 atm.; *o*-cresol, p_c 49·4±0·5 atm.; *p*-cresol, p_c 50·8±0·5 atm.; ethyl bromide, p_c 61·5±0·5 atm.; monomethylaniline, p_c 51·3±0·5 atm. The values have been used for testing some of the numerous formulæ connecting these values with other physical properties. J. F. S.

Thermal Data relating to Condensed Hydrogen. FRANZ SIMON and FRITZ LANGE (*Z. Physik*, 1923, **15**, 312—321).—A comparatively simple form of thermostat for attaining, by the use of liquid hydrogen, temperatures down to 9° abs. is described, and its application to determine thermal data relating to liquid and solid hydrogen detailed. The authors find that the molecular heat of solid hydrogen can be expressed in terms of the absolute temperature by means of a single Debye function, taking $\beta\nu$=91, the limit of error being ±1·5%. The result indicates that solid hydrogen must be considered thermally as monatomic. Within the same limit of error, the molecular heat of liquid hydrogen between 15° and 19° abs. is expressed in terms of the absolute temperature T by $0{\cdot}33+0{\cdot}206T$. The molecular heat of fusion is $28{\cdot}0\pm0{\cdot}1_5$ cals., and the molecular heat of evaporation of liquid hydrogen between 14° and 20° abs. is represented by $219{\cdot}7-0{\cdot}27\,(T-16{\cdot}6)^2\pm1{\cdot}1$ cals. J. S. G. T.

The Chemical Constant of Hydrogen. FRANZ SIMON (*Z. Physik*, 1923, **15**, 307—311).—Thermal data relating to solid hydrogen determined by Simon and Lange (cf. preceding abstract) are applied to calculate the value of the chemical constant of hydrogen. The value so calculated for C is $-1{\cdot}11_1\pm0{\cdot}030$ which leads to the value $C_0(=C-1{\cdot}5\log M)-1{\cdot}56_7\pm0{\cdot}030$, which is in close agreement with the theoretical value, $C_0=-1{\cdot}588$. Values of the vapour pressure of solid hydrogen in cm. of mercury between 7° and 13·94° abs. are calculated by means of the formula $\log p=-\frac{40{\cdot}123}{T}+2{\cdot}5\log T-\frac{1}{4{\cdot}571}\int_0^T\frac{E(91)}{T^2}dT+5{\cdot}30+10^{-10}T^6+3{\cdot}67\times10^{-11}T^7+0{\cdot}7700$, where T is the absolute temperature and E (91) the Debye function taking $\beta\nu$=91. J. S. G. T.

Influence of Surface Tension on Melting and Freezing. ERNST RIE (*Z. physikal. Chem.*, 1923, **104**, 354—362).—A theoretical paper in which, after a general survey of the influence of surface tension on the melting and freezing points, it is shown that the thermodynamic investigations of Pavlov (A., 1909, ii, 19, 295; 1910, ii, 1033) on this subject are untenable. The influence of surface tension on the melting point has been developed thermodynamically, and formulæ have been deduced showing the change in melting point. One of these has the form $T_K - T_0 = 2S_{2,3}T_0/s_3qr$, where T_K is the melting point when the surface tension is taken into account, T_0 when the surface tension is neglected, $S_{2,3}$, is the free energy per unit surface at the interface liquid solid, s_3 is the density of the solid phase, q, the latent heat of fusion, and r the radius of curvature of the solid particle. It is shown that a liquid may be supercooled, but only in exceptional cases may a solid be superheated. The indefiniteness of the melting point of amorphous substances, and particularly of crypto-crystalline substances, is explained by the variation of the size of the particles. A new hypothesis of the structure of glasses is put forward, which differs from that put forward by Tammann ("Metallographic," Leipzig, 1914). The points of difference in the two hypotheses are discussed, and an experimental method of deciding between the two hypotheses is indicated. J. F. S.

Theory of Electrolytes. Lowering of the Freezing Point and Related Phenomena. P. DEBYE and E. HÜCKEL (*Physikal. Z.*, 1923, **24**, 185—206).—A mathematical paper in which the authors discuss the physico-chemical properties of electrolytes in connexion with the theory of electrolytes. Among other results, the following statements are arrived at. 1. For all electrolytes in low concentrations the percentage divergence of the lowering of the freezing point from the classical value is proportional to the square root of the concentration. 2. If the dissolved molecule dissociates into $v_i \ldots v_s$ ions of different kinds with valencies $z_i \ldots z_s$, then for dilute solutions the percentage divergence of the lowering of the freezing point from the classical value is proportional to a valency factor w, where $w = (\Sigma v_i z_i^2)^{3/2}/(\Sigma v_i)^{3/2}$. 3. For dilute solutions, the percentage divergence of the lowering of the freezing point from the classical value is inversely proportional to the three halves power of the dielectric constant of the solvent. These three statements represent limiting conditions. The authors are of the opinion that their calculations fully confirm the hypothesis that the strong electrolytes are completely ionised in solution. J. F. S.

Fused Salts. II. W. HERZ (*Z. Elektrochem.*, 1923, **29**, 274—276; cf. A., 1922, ii, 739).—Using Stefan's formula for the internal pressure of a liquid expressed in terms of the latent heat of evaporation and the specific volume of the liquid, values are deduced for the respective internal pressures of the fused halide salts of lithium, sodium, potassium, rubidium, and cæsium. The values range from 7,650 atmospheres in the case of rubidium iodide to 59,800

atmospheres for lithium fluoride. Cæsium iodide is the only exception to the rule that the value of the internal pressure decreases with increase of atomic weight of either the alkali or halide constituent of the salt, the value in this case being too high to conform with the rule. Values of the diameters of molecules of the respective fused salts, calculated by means of Ostwald's formula, range from $0\cdot23\times10^{-8}$ cm. in the case of lithium fluoride to $0\cdot56\times10^{-8}$ cm. for cæsium bromide. The values, generally, are of the order of one-half or one-third those calculated by Lorenz. The product of the coefficients of thermal expansion of the fused salts and their respective boiling points on the absolute scale is very approximately a constant. Values of the respective critical pressures of the fused salts calculated by the application of Walden's formula (A., 1909, ii, 547) must be regarded only as lower limits, as molecular association occurs in the fused salts. J. S. G. T.

Vapour Pressure and Density of Sodium Chloride Solutions. W. R. BOUSFIELD and C. ELSPETH BOUSFIELD (*Proc. Roy. Soc.*, 1923, [*A*], **103**, 429—443).—Standard values of the respective vapour pressures and densities of aqueous solutions of sodium chloride at 18° are given for the whole range of possible concentrations, viz., 0—26% of sodium chloride by weight. *P* denoting the percentage of sodium chloride, *p* the vapour pressure of water at 18°, taken as 15·383 mm. of mercury, and δp the lowering of vapour pressure due to solution of sodium chloride, the authors find: for $P=26\cdot05$ to $22\cdot45$, $\delta p/p=0\cdot0363+0\cdot00694P+0\cdot0001434P^2$; for $P=22\cdot45$ to $14\cdot90$, $\delta p/p=0\cdot0263+0\cdot0016P+0\cdot0002576P^2$; for $P=14\cdot90$ to $6\cdot92$, $\delta p/p=0\cdot0051+0\cdot00437P+0\cdot0001666P^2$; for $P=5\cdot55$ to $1\cdot40$, $\delta p/p=0\cdot00613P+0\cdot000012P^2$. The values of the density, P_{18}, of the solutions at 18° are given by the relation $P_{18}=0\cdot99862+0\cdot007112P+0\cdot0000168P_2$, correctly to within $\pm0\cdot00002$. A simple method, for the determination of approximate values of the molecular weights of substances, based on the result that for values of *P* between 1 and 5%, the values of dp/p and of *P* are nearly proportional to $\delta \rho$ is described.

J. S. G. T.

Polysaccharides. XIX. The Heats of Combustion of the Carbohydrates. P. KARRER and W. FIORONI (*Helv. Chim. Acta*, 1923, **6**, 396—401; cf. A., 1922, i, 1119).—The heat of combustion of lactose has been redetermined, and the value found, 3948 cal., agrees well with those for maltose (3949), cellobiose (3944), and sucrose (3945). The values found for lactose acetate (4466) and for sucrose octa-acetate (4472) agree well with the calculated value, 4465, for the octa-acetates of the disaccharides. The heat of combustion of anhydrous galactose found, 3720 to 3723·8, is about 20 cal. lower than the values for dextrose and lævulose, possibly on account of the difficulty of obtaining it quite free from water. The value found for galactose penta-acetate (4422·5) is, however, practically identical with that of glucose penta-acetate (4424·5). The heat of combustion of lævoglucosantriacetate, 4530·5, agrees well with the value calculated from that of lævoglucosan, 4533.

Glucose-$\alpha\beta$-anhydride-3 : 5 : 6-triacetate gave the value 4594·8, in accordance with the rule that α-anhydrides have higher heats of combustion. The heat of combustion of glucosan should show whether or no it is an α-anhydride, but attempts to obtain it in a pure crystalline condition suitable for the work by the dehydration of dextrose were not successful. The heats of combustion do not support the opinion of Haworth and Law (T., 1916, **109**, 1314) that lævulose and sucrose contain an ethylene oxide group.

The heat of combustion of rhamnose is 4379 cal.; rhamnose triacetate, 4654·8 cal. (calc. 4643); arabinose, 3731 cal.; xylose, 3735 cal.; xylan, 4242·8 cal.; xylan diacetate, 4548 to 4535 cal. The value for xylan calculated from xylose is 4260 cal. and from xylan diacetate 4266 cal., so the value found is evidently too low, probably on account of impurity in the xylan used for the determination. E. H. R.

Free Energy and Heat of Formation of Zinc Iodide. T. J. Webb (*J. Physical Chem.*, 1923, **27**, 448—454).—With the object of determining the heat of formation of zinc iodide and with the further object of testing the Nernst heat theorem, the author has measured the *E.M.F.* of the cell $ZnHg(10\%)|ZnI_2(sat)||AgI.Ag$ at 25° and 18°. The decrease of the free energy and the temperature coefficient of the free energy have been calculated from the *E.M.F.* measurements. The *E.M.F.* of the cell is found to be 0·39872 volt at 25° and 0·39938 volt at 18°, and the temperature coefficient $-0·000094$ volt/degree, which gives the value 19·7 Cal. as the heat of the reaction $Zn+2AgI=ZnI_2+2Ag$. Since the heat of formation of two molecules of silver iodide is 30·2 Cal., the heat of formation of zinc iodide is 49·9 Cal. A direct calorimetric determination of the heat of formation of zinc iodide has been carried out and the value 49·8 Cal. obtained. The heat of solution of zinc iodide is found to be $11·6\pm0·3$ Cal. J. F. S.

The Heat of Formation of some Isomorphous Mixtures of Organic Compounds. N. N. Nagornov (*J. Russ. Phys. Chem. Soc.*, 1919, **51**, 301—310).—The heats of formation of the following pairs of organic compounds which are known to form isomorphous mixtures were determined: chlorocinnamaldehyde and bromocinnamaldehyde; *p*-dichloro- and *p*-dibromo-benzenes; and *p*-dichloro- and *p*-chloroiodo-benzenes. The method of investigation consisted in observing the difference in the heat of solution in benzene of the isomorphous mixtures (prepared by melting together the components and subsequently powdering the fused mass) and ordinary mixtures of the compounds in question. It is shown that these isomorphous mixtures, like those of inorganic salts, are produced with absorption of heat which is least in the first pair of substances, the mixture of which shows a liquidus curve above the straight line joining their melting point (Küster, A., 1892, 396); it is greatest in the third pair of substances the mixture of which shows a liquidus curve passing through a minimum below the melting point of the more fusible component (A., 1911, i, 27). The system naphthalene–*m*-dinitrobenzene

which forms a definite compound was also investigated, and it is shown that when the components are melted together in the correct proportions the heat of solution of the product differs from that of a mechanical mixture; the compound is, however, completely dissociated in benzene solution; the heat of formation of the compound is −165 cal. The system naphthalene-*p*-dibromobenzene, which merely forms a eutectic corresponding with 40% naphthalene, was investigated for comparison; the formation of the eutectic is found to be unaccompanied by any absorption of heat.

G. A. R. K.

Some Density Determinations. A. C. EGERTON and W. B. LEE (*Proc. Roy. Soc.*, 1923, [*A*], **103**, 487—499).—The accuracy of the Archimedes method of determining densities is increased by using certain mobile and heavy organic liquids such as ethylene dibromide and carbon tetrachloride, which reduce air-bubble difficulties and damping. The respective boiling points, at 760 mm. pressure, of ethylene dibromide and carbon tetrachloride were found to be 131·65±0·1° and 76·7±0·1°. The following values were found for the density of ethylene dibromide at the various temperatures specified: 15·68°, 2·188632; 16·26°, 2·187440; 16·87°, 2·186211; 17·33°, 2·185210; 17·79°, 2·184333; 18·29°, 2·183243; 18·95°, 2·181847; 19·51°, 2·180750. The results are probably correct to within 0·000005. Corresponding results for carbon tetrachloride were obtained as follows: 15·67°, 1·60258; 16·10°, 1·60182; 16·49°, 1·60100; 17·15°, 1·59982; 17·75°, 1·59834; 18·26°, 1·59753; and are probably correct to 0·00005. A method of preparing a sample of lead or cadmium suitable for the determination of density, and involving filtering, casting, and heating the metal in a vacuum is described. From nine determinations on three different samples of metal, the density of lead at 20° was found to be 11·3437, correct to 1 part in 100,000 parts. Values of the density of uranium lead, determined at 16·3°, were 11·2957 and 11·2962, corresponding with an atomic weight of the metal equal to 206·26. The value of the density of cadmium was found to be influenced by the treatment the metal had undergone. Values determined at 16·3° ranged from 8·6435 to 8·6557. Values, consistent to within 1 part in 20,000, were obtained by employing 1·5 g. of the metal.

J. S. G. T.

The Pressure of Gaseous Mixtures. I. MASSON and L. G. F. DOLLEY (*Proc. Roy. Soc.*, 1923, [*A*], **103**, 524—538).—With a view to determine the validity or otherwise of the laws of additive volumes and pressures in the case of binary mixtures of gases, the authors have investigated the isothermal behaviour at 25° of mixtures of ethylene, argon, and oxygen at pressures up to 125 atmospheres. The results indicate that the volume of an argon-ethylene mixture is usually markedly greater than the sum of the separate volumes, all being measured at the same pressure. The maximum relative difference occurs at a mixture-pressure of about 75 atmospheres. With a fixed mixture-pressure there is a

particular molecular ratio for which the difference attains a maximum positive value. This optimum ratio depends on the mixture-pressure and varies between about 75 and 45 molecules of ethylene %. Mixtures rich in ethylene and measured at the higher pressures approach the additive volume more nearly and eventually the volume-differences become negative. In the case of argon-oxygen mixtures, a very small positive difference in total volume is found. When oxygen is mixed with ethylene, the volume differences are slightly larger than those occurring in the case of argon-ethylene mixtures. In the case of argon-ethylene mixtures rich in ethylene and under high pressures, the total pressure is greater than the sum of those of the constituents taken separately. At moderate densities, where the mixtures are less rich in ethylene or under lower pressures, the pressure of the mixture is less than the additive value. In the case of argon-oxygen mixtures, the deviations from the additive value of the pressure are much smaller than those characterising the ethylene-argon mixtures, and their sign is that of a cohesion effect, tending towards an upper limit. With oxygen-ethylene mixtures, the deviations of pressures approximate to those of the corresponding argon-ethylene mixtures. The maximum decrease from the additive value occurs at an optimum molecular composition of 50—60% of ethylene. The results indicate that whilst both the law of additive volumes and the law of additive pressures are invalid, the former is the more inaccurate. The latter fails because it neglects the fact that the space in which each gas is enclosed is already partly filled by molecules of the other, and because no allowance is made for the mutual attraction between molecules of one constituent and those of the other. The attractions of oxygen and argon molecules for ethylene molecules are substantially the same. Assuming that internal pressure or cohesion in a gas of moderate density is due partly to the formation of molecular aggregates of varying complexity, the authors conclude that at the ordinary temperature these complexes are in reversible equilibrium with their original constituents. Regarded from the point of view of the current electronic theory of molecular structure, it would appear that molecular cohesion between any two gases would be that of the gas or gases of the argon group the electronic configurations of which the gases simulate. J. S. G. T.

The Viscosity of Lubricating Oils at Low Temperatures. MASATOSHI OKOCHI and MASAICHI MAJIMA (*Rikwagaku Kenkyujo Ihô*, 1923, **2**, 23—37).—The viscosity was measured by passing the oil through a glass capillary (10 cm. long) by the aid of suction or of compressed air, at temperatures varying from 27° to −18°. From the data, the viscosities were calculated by the formula: $\eta=\pi R^4/8Vl\,.\,(P_e-P_i)$, where R=radius of the capillary, V=volume of oil flowing through the capillary, l=length of the capillary, and P_e and P_i=pressures of the oil at the exit and entrance of the capillary. The results were given in tables and diagrams. The oils used for the investigation were as follows: (1) rape seed-, (2) gingell-, (3) refined rape seed-, (4) camellia-, (5) mobile-,

(6) soja bean-, (7) spindle-, (8) whale-, (9) olive-, and (10) machine-oils, (11) petroleum, (12) liquid paraffin, and some mixtures. The increase of viscosity owing to the decrease of temperature is almost expressed by hyperbola; the formula $\eta=(a/T-b)^{1/\alpha}$ is proposed, where α, a, and b are constants. The values of η calculated from the formula are almost identical with the experimental figures. But in (2), (6), and (8), they do not coincide at low temperatures, and some critical temperatures were observed, due to the formation of solid particles. The increase of η of petroleum by lowering the temperature is very small, and η with other oils is decreased by addition of petroleum. K. K.

Sorption Capacity of Carbon. J. B. Firth (*J. Soc. Chem. Ind.*, 1923, **42**, 242—244T).—The author has investigated the sorptive power and catalytic activity of carbon prepared in various ways. Six different varieties of carbon were prepared and examined. (1) Sucrose was carbonised at as low a temperature as possible and the product purified; (2) material obtained as above was heated in a vacuum for two hours at 600°; (3) material as in (1) was heated at 900° for two hours in a vacuum; (4) a solution of 100 g. of sucrose in 100 c.c. of water was mixed with 50 g. of zinc chloride in 100 c.c. of water, evaporated to dryness, and carbonised. The material was purified with hydrochloric acid and washed until all chloride had been removed, dried, and heated in a vacuum at 600° for two hours; (5) fifty g. of zinc chloride were melted and 100 g. of sucrose slowly added; the resulting carbon was purified; (6) fifty g. of pure kieselguhr were made into a paste with a concentrated solution of sucrose, dried, and carbonised. The six forms were then treated with 25 c.c. of $N/10$-iodine solution and the amount sorbed determined after five minutes, thirty minutes, two hours, and twenty-four hours. The results show that the activity is much improved by heat treatment and by the mixing with kieselguhr and zinc chlorides. The catalytic activity of varieties (1), (2), and (3) was compared by measuring the decomposition of hydrogen peroxide at 18° in the presence of these substances. The results show that the catalytic activity is increased by heat treatment and that the activity gradually decreases as the reaction progresses. On keeping, the activity of the carbon appears to decay, and the decay becomes more permanent the longer the carbon is preserved. The increased activity is attributed by the author to the breaking down of complex carbon molecules into something simpler and so increasing the attractive force. J. F. S.

Adsorption by Activated Sugar Charcoal. II. F. E. Bartell and E. J. Miller (*J. Amer. Chem. Soc.*, 1923, **45**, 1106—1115; cf. A., 1922, ii, 741).—The hydrolytic adsorption of sodium picrate, ammonium picrate, sodium eosin, and ammonium eosin by ash-free sugar charcoal, and the relative adsorption of a number of acids and bases by the same adsorbent has been determined, and finally the change in the hydrogen-ion concentration of a number of aqueous solutions of salts due to adsorption has also been

determined. It is shown that the adsorption of acid dyes is accompanied by considerable hydrolysis and liberation of alkali hydroxide, which remains in solution. Ashless sugar charcoal does not adsorb the strong inorganic bases. The adsorption of a salt of a strong base and a readily adsorbed acid results in hydrolysis and the liberation of the free base. The effect on adsorption of the substitution of hydroxyl and amino-groups in organic acids has been investigated, and it is shown that the introduction of the hydroxyl group decreases the adsorption of the acid to a more or less marked extent, depending on the nature of the acid into which it is introduced. The introduction of the amino-group decreases the adsorption of the acid, the extent also depending on the nature of the acid into which it is introduced. The effect of the amino-group is considerably greater than that of the hydroxyl group. A number of the conflicting results of other investigators have been reproduced by means of neutral, activated, ash-free charcoal and an explanation of their causes has been advanced. J. F. S.

Adsorption of Silver Salts on Silver and Gold Surfaces. E. G. RUDBERG and H. VON EULER (*Z. Physik*, 1923, **13**, 275—283; cf. this vol., ii, 13).—The amount of silver-ion adsorbed per square metre of surface reaches a maximum at a silver-ion concentration about 0·03 *N*. The silver is possibly attached to the silver surface according to the equation $Ag+Ag^{\cdot}=Ag_2^{\cdot}$. The amount of adsorption is independent of temperature, and is the same from aqueous as from alcoholic (96%) solutions. No detectable adsorption was observed when the metals were placed in dilute solutions of sodium sulphate or sulphuric acid. Ammonium thiocyanate is adsorbed by an oxidised silver surface, but not by a clean surface. Probable values for the diameter of the adsorbed silver-ions are discussed (cf. this vol., ii, 13). W. E. G.

The Adsorptive Power of Aluminium Hydroxide. I and II. H. VON EULER and ELSA ERIKSON (*Z. physiol. Chem.*, 1923, **128**, 1—8, 9—13).—Aluminium hydroxide prepared according to the method of Willstätter and Racke (A., 1922, i, 823) does not absorb sucrose at p_H 6·5. Less than 1% of leucine is adsorbed by 3·3 g. of aluminium hydroxide from a 0·08/*N*-solution of that amino-acid of p_H 5·4—9·0. The adsorption of nucleic acid depends on the p_H and varies from 0·61 g. of sodium nucleate per 1 g. of aluminium hydroxide at p_H 3·5 to 0·33 g. at p_H 7·6. At a p_H 5·7, the adsorption of phosphate is not complete within twenty-six hours. The adsorption reaches a maximum at p_H about 3·2, when 0·426 g. PO_4 is absorbed per 1 g. of aluminium hydroxide. At p_H 4·9, 0·401 g. is adsorbed and at p_H 2, 0·330 g. W. O. K.

Negative Adsorption. III. Action of Gelatin on Sodium Chloride Solution. M. A. RAKUSIN and TATIANA GÖNKE. **IV. Action of Gelatin on Acids.** M. A. RAKUSIN and TATIANA GÖNKE. **V. Action of Agar-agar on Ammonium Chloride Solution.** M. A. RAKUSIN. **VI. Action of Gelatin on Aqueous Ethyl Alcohol.** M. A. RAKUSIN and TATIANA GÖNKE (*Biochem. Z.*, 1923, **137**, 341—355).—Aqueous solutions of a variety of sub-

stances acting on air-dry gelatin increase in concentration as shown by density determinations. Some gelatin passes into solution, but the main effect is attributed to negative adsorption. More exact investigation of the action of sodium chloride on gelatin shows that the actual concentration of chloridion falls off, the increased density being due to gelatin. Similarly, five organic and four inorganic acids exposed to gelatin show a falling off of titre. The falling off of the concentration of ammonium chloride solution when exposed to agar-agar containing 19% of water is due to dilution by the water of the agar-agar. When air-dried gelatin was exposed to aqueous alcohols containing more than 40% of alcohol there was no change of density of the solutions, but weaker solutions increase in density through solution of the gelatin. H. K.

Osmotic Pressure. I, II, and III. MICHAIL KIRIANOVITSCH LEVALT-EZERSKI (*J. Russ. Phys. Chem. Soc.*, 1920, **51**, 231—241, 241—244).—II. Two formulæ are deduced for the osmotic pressures of solutions—Schiller's formula, $P=(p_0-p)s/\sigma$, where P is the osmotic pressure, p_0 and p are the vapour pressures of the solvent and the solution, respectively, and s and σ the relative volumes of the vaporised solvent and the solution, respectively, and Kistiakovski's formula (A., 1899, ii, 730), $P=p_0v_0/\sigma_0 ln\,.\,p_0/p+p-p_0$, where v_0 and σ_0 are the relative volumes of the vaporised and liquid solvent, respectively, and l and n are constants. These formulæ are shown to approximate very closely to each other at low concentrations. Experimentally-determined values for the osmotic pressures of sucrose solutions are in good agreement with those calculated from Schiller's formula, up to 70 atmos.; but no similar agreement exists for solutes other than sucrose. A simple linear relation exists between the osmotic pressure of a solution and the depression of freezing point produced by the solute, the osmotic pressure being 11·898 atmospheres for each degree of depression of freezing point of water by the addition of sucrose. For electrolytes, this relation is modified, and the osmotic pressure is then given by the formula $P=P_{calc.}t_{exp.}/t_{calc.}$, where $P_{calc.}$ is the osmotic pressure calculated for non-electrolytes, $t_{calc.}$ the depression of freezing point calculated from the formula $t=Em/M$, and $t_{exp.}$ the depression of freezing point found experimentally. Osmotic pressures of aqueous solutions of sodium chloride, nitrite, and hydroxide, and calcium chloride calculated from this formula agree well with experimental values.

III. The importance of the relation between osmotic pressure and depression of freezing point of aqueous solutions, $P=11{\cdot}9\delta$, where P is the osmotic pressure in atm. and δ the depression in degrees, and the desirability of obtaining similar relations for other solvents, are pointed out. It is surmised that the factor 11·9 is connected with the latent heat of liquefaction of ice, and it is shown that the accepted molecular depression for water (1·86), if divided into the molecular volume (22·4 l.) gives a value differing only by 0·14 from the above factor. R. T.

Thermodynamics of Activity and Osmotic Coefficients. NIELS BJERRUM (*Z. physikal. Chem.*, 1923, **104**, 406—432).—A theoretical paper in which several forms of the Gibbs's differential equation between the affinities of the components of a mixture have been put forward. It is shown that these may be deduced in a simple direct manner from the second law of thermodynamics. The main point of Gibbs's equation is stated as follows. The work required to transform a finite quantity of a mixture into one which differs from it to an infinitely small extent is infinitely small. From this statement, the various forms of Gibbs's equation may be directly deduced. The different possibilities in defining the activity coefficient f and the osmotic coefficient ϕ are pointed out and emphasised. The method of deduction and the limits of applicability of the equation $1+cd\log_e f/dc=\phi+cd\phi/dc$, previously deduced (A., 1919, ii, 9), are discussed and it is shown that this equation is applicable up to the highest concentration when the concentration, C, is expressed in g. mols. per litre of solvent. Similar equations for solutions of several substances are deduced. If f_i and f_k are the activity coefficients of the components S_i and S_k and c_i and c_k their concentrations, then $\delta f_i/\delta c_k=\delta f_k/\delta c_i$. The significance of this equation for the deduction of equations for ionic activity coefficients is pointed out and illustrated by examples. It is further shown that it is possible to resolve the osmotic pressure into a number of osmotic partial pressures, and osmotic coefficients can be deduced for each component of a solution of several substances exactly as is the case with the activity coefficients. It is shown to be impossible to determine the partial osmotic pressures by means of semi-permeable membranes. J. F. S.

Mutual Solubility of Liquids. I. Mutual Solubility of Ethyl Ether and Water. II. Solubility of Water in Benzene. ARTHUR E. HILL (*J. Amer. Chem. Soc.*, 1923, **45**, 1143—1155).—The author describes two new methods for the determination of the mutual solubility of liquids in one another. The first method depends in the application of the phase rule to the volumes obtained by mixing the two liquids in two different ratios by weight, in two separate experiments at the same temperature. If m and m' are the weights of the first component used in the two experiments, x is its concentration in g. per c.c. at equilibrium in the upper phase in both experiments, and y its concentration in the lower phase. If now a and a' are the measured volumes of the two upper phases at equilibrium and b and b' those of the lower phases, then it follows that $ax+by=m$ and $a'x+b'y=m'$, so that x and y, the concentration of the first component in g. per c.c., is known in each phase by solving the two equations. If now n and n', the weights of the second component, are used instead of m and m' in the equations, the concentrations of this component in the two phases are also known. By adding together the weight of each component in 1 c.c. of a given phase, the density of that phase at once follows, and consequently the mutual solubility in g. per gram can be calculated. This method is carried out in a double

flask, the lower bulb of which has a capacity of 100 c.c. or 300 c.c. and the upper bulb of 300 c.c. or 100 c.c. The two bulbs are connected by a tube 1 cm. diam. of 5 c.c. capacity graduated in 1/10 c.c., and the upper flask has a graduated neck of the same type. Suitable volumes of the liquids are placed in the flasks and shaken at the required temperature, allowed to settle, and the volumes measured. Using this method, the mutual solubility of ether and water has been determined at −3·83°, 0°, 10°, 15°, 20°, and 25°, with the following results: ether layer contains 1·409% of water at 30°, 1·338% at 25°, 1·264% at 20°, 1·240% at 15°, 1·164% at 10°, 1·078% at 0°, and 0·978% at −3·83°. The water layer contains 5·340% of ether at 30°, 6·027% at 25°, 6·896% at 20°, 7·913% at 15°, 9·040% at 10°, 11·668% at 0°, and 12·752% at −3·83°. The second method, whilst not so generally applicable, can nevertheless be used for many pairs of liquids. The method depends on the solubility of silver perchlorate in many organic solvents; this solubility is much increased by the presence of traces of water in the solvents. The method consists in making a curve of the solubility of silver perchlorate in a given organic solvent which contains known amounts of water and then saturating that solvent with water and determining the solubility of the perchlorate in the saturated solution and deducing the solubility of water in the solvent from the curve. The solubility of water in organic solvents is much increased by the presence of silver perchlorate so that the reference curve can be drawn far beyond the water concentration represented by the solution saturated with water. This method has been applied to the determination of the solubility of water in benzene and the following results have been obtained: 5·4°, 0·034%, 15·0°, 0·054%, 25°, 0·073%, 37·5°, 0·115%, 50°, 0·156%, 57·5°, 0·185%, 65°, 0·230%, and 69·5°, 0·265%. J. F. S.

A Critical Solution Temperature for Solids in the Binary System Ammonium Chloride–Manganous Chloride Dihydrate. FREDERICK WILLIAM JEFFREY CLENDINNEN and ALBERT CHERBURY DAVID RIVETT (T., 1923, **123**, 1344—1351).

Binary Critical Solution Temperatures as Criteria of the Purity of Acetic Acid. DAVID CHARLES JONES (T., 1923, **123**, 1374—1384).

Ternary Critical Solution Temperatures as Criteria of Liquid Purity. DAVID CHARLES JONES (T., 1923, **123**, 1384—1395).

Molecular and Crystal Symmetry. JOHN W. EVANS (*Nature*, 1923, **111**, 740); G. SHEARER and W. T. ASTBURY (*ibid.*, 740—741).—Comments on, and a reply to Barker's note (this vol., ii, 388). A. A. E.

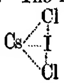
The Abnormal Reflection of X-Rays by Crystals. GEORGE L. CLARK and WILLIAM DUANE (*Proc. Nat. Acad. Sci.*, 1923, **9**, 131—135).—Further details are given of the *X*-peak reflections, characteristic of one of the chemical elements in the crystal examined

(cf. A., 1922, ii, 483). The value for the wave-lengths producing these peaks is obtained by determining the critical voltage below which the reflections do not occur. For potassium iodide, this voltage corresponds with the critical voltage for the *K*-series of iodine. Some of these reflections obey the law $n\lambda=2d\sin\theta$ (cf. following abstract). Others, however, are reflected abnormally and do not obey this law. The peaks for these reflections are smaller than the normal *X*-peaks, and there are always two of these, on the two sides of the peak representing reflection from the 100 planes and at equal angles from it. The same is true for the 010 planes and the 001 planes. No adequate explanation has yet been found for this peculiar reflection in the *X*-peak.

W. E. G.

The Reflection by a Crystal of *X*-Rays Characteristic of Chemical Elements in it. GEORGE L. CLARK and WILLIAM DUANE (*Proc. Nat. Acad. Sci.*, 1923, 9, 126—130).—By the method previously described (preceding abstract) the *X*-rays characteristic of cæsium, iodine, and bromine have been identified. These rays produced by the excitation of atoms in crystals obey the law $n\lambda=2d\sin\theta$. By the critical voltage method, the 100 and 110 planes of potassium iodide yield values characteristic of iodine which agree very closely with the true values. With the tri-iodide the same kind of iodine spectra have been obtained. Assuming the wave-lengths corresponding with the peaks, the distance between the iodine planes may be calculated from the equation $n\lambda=2d\sin\theta$, and it is shown that the original unit cube of KI with $d=0.3532$ Å. has expanded to an edge length of 0·470 Å. For cæsium, four orders of characteristic cæsium peaks appear, together with the values for I_α and I_β, and it becomes possible to analyse separately the space distributions of both the cæsium and iodine atoms. d_{010} for cæsium is 0·643 Å., and for iodine 0·1609 Å.; hence planes containing iodine atoms are one-fourth as far apart as those containing cæsium atoms. From the similar results obtained for other planes it is deduced that the crystal unit for CsI_3 is a rectangular parallelopiped with cæsium atoms at the corners, and iodine atoms at the centre and equidistant along the body diagonal. $CsIBr_2$ has also been investigated with similar results. W. E. G.

The Significance of the Experimentally Determined Crystal Structures of the Alkali Polyhalides. G. L. CLARK (*Proc. Nat. Acad. Sci.*, 1923, 9, 117—122).—A *résumé* of the previous work on the polyhalides (cf. Clark and Duane, A., 1922, ii, 483, also preceding abstracts, and Wyckoff, A., 1923, ii, 311). The crystal structures of polyhalides, KI_3, CsI_3, $CsIBr_2$, $CsICl_2$, have now been determined, and, in spite of the fact that three crystallographic systems are represented, the atoms are arranged in the same manner in unit parallelopipeda in all four cases. The metal atoms occupy the corners of the cell, and the halogen atoms, positions inside the cell on the body diagonal with the heaviest atom in the centre. The structure is closely related to the simple halide unit cube, the dimensions being changed, and the cubic symmetry

destroyed. The halogen atoms constitute a singly acting group just as truly as they do in the formation of complex ions in solution. The stability of the polyhalides is directly proportional to the atomic volumes of the metals. Thus the polyhalides of sodium do not exist, and only the polyiodide of potassium is stable. From the size of the unit cell, it is shown that the atoms in the I_3 group are considerably flattened in the direction parallel to the cell diagonal. The nearest approach to a mechanical formulation of $CsICl_2$ is  W. E. G.

The Properties of some Silver Organosols. JOHN KENNETH GILES and CYRIL SEBASTIAN SALMON (T., 1923, **123**, 1597—1608).

The Protective Action of Potassium Oleate on Gold Sols in Water-Alcohol Mixtures. ERIC KEIGHTLEY RIDEAL and LOUIS LEIGHTON BIRCUMSHAW (T., 1923, **123**, 1565—1570).

The Theory of Gels. IV. SAMUEL CLEMENT BRADFORD (*Biochem. J.*, 1923, **17**, 230—239).—Granules composing jellies of gelatin and agar are spherites. These gelatin spherites give the shadow-cross in polarised light. The author concludes that the forces which hold gelatin and agar in solution are the same as those that operate between other solutes and solvents, and that the setting of jellies of the natural emulsoids is merely a process of crystallisation. S. S. Z.

Purification of Liquids by the Simultaneous Action of Centrifugal Force and an Electrical Field. ALFRED MARX and JEAN ROZIÈRES (*Compt. rend.*, 1923, **176**, 1396—1398).—No satisfactory method of separating from a liquid a colloid held in suspension has been devised either in the nature of centrifugal or electrical action. By a combination of these two methods, the authors have effected complete separation in a short space of time, employing a potential difference of 40,000 volts and a speed of 2700 revolutions per minute. Details of the apparatus and methods of working are given, together with some observations which indicate the efficiency of the process. H. J. E.

The Swelling of Agar-agar. FRED FAIRBROTHER and HAROLD MASTIN (T., 1923, **123**, 1412—1424).

Relation of Hydrogen-ion Concentration to the Flocculation of a Colloidal Clay. RICHARD BRADFIELD (*J. Amer. Chem. Soc.*, 1923, **45**, 1243—1250).—The amount of electrolyte necessary to flocculate colloidal clay has been determined in the case of hydrochloric, sulphuric, phosphoric, acetic and citric acids, potassium chloride, and dipotassium phosphate. The hydrogen-ion concentration of the solutions in which flocculation took place has been determined both electrometrically and by the indicator method. The results show that with the exception of citric acid the acids flocculate the clay at about the same Sörensen value,

but with citric acid a greater acidity was necessary. Changes in the Sörensen value from 6·2 to 8·0 increased the electrolyte requirement ten times in the case of mixtures of potassium chloride and hydroxide. Further increases in alkalinity were without effect. Dipotassium phosphate mixtures showed a similar variation in flocculating power with changes in hydrogen-ion concentration. The phosphate curves differ, however, from the chloride curves in three respects, namely, the break occurs in more acid mixtures, the amount of electrolyte required is greater, and the curve shows a second minimum in alkaline mixtures. The general results indicate that the flocculating power of potassium salts is strongly influenced by the nature of the anion, even when they are compared at the same Sörensen values. Secondary reactions appear to be responsible.

J. F. S.

Equilibrium of Steam in the Presence of Iron and Tungsten and Oxides of these Metals. LOTHAR WÖHLER and R. GÜNTHER (*Z. Elektrochem.*, 1923, **29**, 276—285).—The authors have investigated the equilibrium of iron and steam in the presence of the respective phases Fe/FeO, FeO/Fe_3O_4, and Fe_3O_4/Fe_2O_3, employing both the process of oxidation and of reduction to attain equilibrium. Below 570°, the authors find, in agreement with the results of Reinders and van Groningen (A., 1922, ii, 153) and of Chaudron (A., 1921, ii, 584) that the value of the equilibrium constant K_2 for the phases Fe_3O_4/FeO is the same as the value of K_3 for FeO/Fe. The quadruple point of the system $Fe/FeO/Fe_3O_4/O_2$, below which FeO is unstable and decomposes into Fe and Fe_3O_4, is therefore about 570°. The equation of the reaction isochore for the three systems is deduced in the general form $\log K = C - Q/4{\cdot}571T$, where Q denotes the respective heats of reaction. Combining these equations with the equation representing equilibrium in the dissociation of steam, expressions are deduced representing equilibrium in the dissociation of the various iron oxides. Similarly, expressions are derived for the respective oxygen pressures in the case of the three phases at various temperatures and approximate values calculated for the respective heats of oxidation of the oxides. Values of the *E.M.F.* of oxidation cells employing the phases FeO/Fe and Fe_3O_4/FeO, calculated by the formula $E = 0{\cdot}0002T \log (p_1/p_2)/4$, agree closely with the experimental values found by Treadwell (A., 1917, ii, 117). Conditions are detailed under which the reduction of ferric oxide to pure ferrous oxide by means of a mixture of steam and hydrogen in which the H_2O/H_2 ratio lies between the value of K_2 for Fe_3O_4/FeO and of K_3 for FeO/Fe may be effected. Below 560°, the reduction of Fe_3O_4 proceeds directly to metallic iron. A method of preparing pure tungsten dioxide and pentoxide respectively is described, and the equilibrium constants of steam and the respective phases WO_3/W_2O_5, W_2O_5/WO_2 and WO_2/W are determined. The equations of the respective reaction isochores are given by $\log K_1 = -1375/T + 2{\cdot}235$ for WO_3/W_2O_5; $\log K_2 = -1000/T + 1{\cdot}218$ for W_2O_5/WO_2; and $\log K_3 = -1904/T + 1{\cdot}554$ for WO_2/W. Equations are deduced for the equilibrium

dissociation of the various oxides, and values calculated for the respective oxygen pressures at various temperatures in the case of these as for the iron oxides. J. S. G. T.

The Theory of Acid-Alkali Solution Equilibrium as Applied to Salts of Moderately Strong but Sparingly Soluble Acids. EDMUND BRYDGES RUDHALL PRIDEAUX (T., 1923, **123**, 1624—1634).

Mixed Crystals and Double Salts: A Comparison of Systems Containing Water, Ammonium Chloride, and a Chloride of Manganese, Iron, Cobalt, Nickel, or Copper. ALBERT CHERBURY DAVID RIVETT and FREDERICK WILLIAM JEFFREY CLENDINNEN (T., 1923, **123**, 1634—1640).

Velocity of Chemical Reactions. J. A. CHRISTIANSEN and H. A. KRAMERS (*Z. physikal. Chem.*, 1923, **104**, 451—471).—A theoretical paper in which an hypothesis of unimolecular gas reactions is developed on the basis of an activation of the reacting molecules by the absorption of radiation. J. F. S.

The Propagation of Flame from a Spark in a Closed Tube through a Homogeneous Inflammable Mixture. OLIVER COLIGNY DE CHAMPFLEUR ELLIS (T., 1923, **123**, 1435—1452).

The Formation of the Explosive Wave. P. LAFFITTE (*Compt. rend.*, 1923, **176**, 1392—1395).—The distance traversed by the flame in a mixture of oxygen and carbon disulphide vapour before the starting of an explosion wave depends on the diameter of the tube and the author's experimental results, recorded photographically, are shown in the form of a diagram based on these two factors. The formation of an explosive wave may be advanced or retarded by variations in the composition of the mixture; when these exceeded 1% a change in the experimental values was observed. If the interior of the tube is not perfectly smooth, the transformation from combustion to explosion occurs considerably earlier, usually at the point where the irregularity ceases. H. J. E.

Catalytic Combination of Ethylene and Hydrogen in the Presence of Metallic Copper. Measurements of Reaction Velocity and Adsorption Isotherms at 0° and 20°. ROBERT N. PEASE (*J. Amer. Chem. Soc.*, 1923, **45**, 1196—1210).—The kinetics of the catalytic combination of hydrogen and ethylene in the presence of metallic copper has been investigated at 0° and 20°, and measurements of the velocity of reaction and the adsorption isotherms have been made. It is found that within limits, the velocity increases with the hydrogen concentration but decreases as the ethylene concentration is increased, the particular relation being $\Delta P = KV^{n}_{H_2(total)} \cdot (V_{Sat.} - V_{C_2H_4(ads)})$, in which ΔP is the decrease in pressure from the fifth to the fifteenth minute; $V_{H_2(total)}$ is the initial volume of hydrogen; $V_{Sat.}$ the saturation capacity of the catalyst surface for ethylene; $V_{C_2H_4(ads)}$ the volume of ethylene adsorbed. For the copper catalyst most completely investigated,

$n=0\cdot8$ and $V_{\text{Sat.}}=9\cdot30$ c.c. The expression $V^n_{H_2(\text{total})} \cdot (V_{\text{Sat.}} - V_{C_2H_4(\text{ads})})$ is taken to be proportional to the adsorption of hydrogen in the presence of ethylene. The temperature coefficient of the reaction velocity has been found to be 1·62 for 10° rise between 0° and 20°. It is pointed out that this effectually disposes of the possibility of diffusion playing a dominant part in the process. The similarity between the conclusions drawn in the present work as to the kinetics of the ethylene–hydrogen combination and those of Armstrong and Hilditch as to the catalytic hydrogenation of unsaturated organic liquids is pointed out (A., 1920, ii, 102, 364, 422, 423, 608; 1921, ii, 582; 1922, ii, 41, 756, 757). J. F. S.

Catalytic Decomposition of Hydrogen Peroxide in a Bromine–Bromide Solution, and a Study of the Steady State. William C. Bray and Robert S. Livingston (*J. Amer. Chem. Soc.*, 1923, **45**, 1251—1271).—It has been shown that in acid solution hydrogen peroxide oxidises bromide to bromine and reduces bromine to bromide, and these two reactions can take place independently in the same solution. When the rates of these two compensating reactions are equal, the effective action is the catalytic decomposition of hydrogen peroxide. This constitutes a "steady state" in which the concentrations of bromine, bromide, and acid remain constant in a given experiment. At the steady state, the rate of decomposition of the peroxide in the dark at 25° in sulphuric acid solutions of concentration above $0\cdot2N$ is represented by the equation $-d[H_2O_2]/dt=K[H_2O_2] \cdot [H^{\cdot}] \cdot [Br']$. At the steady state, the functional equation, $R=[Br_2]/[H^{\cdot}]^2 \cdot [Br']^2$, is shown to hold for sulphuric acid concentrations below N, where R is a constant having the value 0·20. The value of R increases slightly with decreasing temperature, but decreases to a very small value when the reaction mixture is exposed to sunlight. Definite evidence that the catalyst is completely accounted for by the two compensating reactions is obtained by measuring the rate of each at a distance from the position of the steady state. The results of these determinations agree closely with those predicted from the steady state-data and the assumption of a kinetic or rate-determining mechanism involving hypobromous acid. The ratio of the specific reaction rates of the two reactions is equal to R, and at the steady state each reaction accounts for half the peroxide decomposed. $H_2O_2+2Br'+2H^{\cdot} \longrightarrow Br_2+2H_2O$; $H_2O_2+Br_2 \longrightarrow O_2+2Br'+2H^{\cdot}$. The possibility of choosing catalysts by means of free-energy data is discussed and some examples of the method of calculation are given. A method is described for the volumetric estimation of hydrogen peroxide in the presence of bromide, which is as follows. To the aqueous solution enough water is added and then sulphuric acid to make the volume about 150 c.c. and the acid concentration $0\cdot3-0\cdot5N$. Then, immediately and rather rapidly, potassium permanganate solution is added until a distinct pink colour remains for two to three seconds. (An excess of $1\cdot0-3\cdot0$ c.c. of $0\cdot1N$-permanganate is recommended.) The solution is stirred vigorously, a moderate excess of potassium iodide solution added, and after waiting a short

time, but in no case longer than a minute, the liberated iodine titrated with thiosulphate. The method is shown to be accurate to within 0·2—0·3%. J. F. S.

Decomposition of Potassium Perchlorate and its Catalysis by Ferric Oxide. CARL E. OTTO and H. SHIPLEY FRY (*J. Amer. Chem. Soc.*, 1923, **45**, 1134—1142).—The rate of decomposition of potassium perchlorate both alone and in the presence of ferric oxide as catalyst has been determined for various amounts of catalyst at temperatures ranging from 450° to 600°. The results show that the reaction is unimolecular and takes place according to the equation $KClO_4=KCl+2O_2$. During the reaction the particles of ferric oxide catalyst increase in size fivefold. There is no evolution of chlorine either in the presence or absence of the catalyst. The velocity coefficient is in keeping with the law of Arrhenius over the range investigated. With ferric oxide as catalyst, the increase in the velocity coefficient at constant temperature is proportional to the weight concentration of the catalyst. The expression $(K_c-K_0)/C$ varies with the temperature in keeping with Arrhenius's law. The above-mentioned results indicate that the addition of the catalyst does not accelerate the reaction already proceeding, but that a concomitant reaction occurs which involves the catalyst, probably in the formation of an intermediate compound, whilst the original reaction proceeds with unchanged velocity. The total velocity is the sum of the velocity of uncatalysed reaction and that of the reaction due to the catalyst. Only the velocity of the latter reaction is influenced by the concentration of the catalyst. This deduction is possible because the decomposition reaction velocities of the catalysed and the uncatalysed decompositions are of the same order of magnitude. From this point of view, an expression like that of Arrhenius has been developed, by which the velocity coefficient under any condition of temperature and concentration of catalyst can be calculated. The expression has the form $K=C\,.\,10^{A/T+B}+10^{A_0/T+B_0}$, where $A=-10587$, $B=11·5679$, $A_0=-13246$, and $B_0=14·0348$. J. F. S.

Oxidation of Copper and the Reduction of Copper Oxide by a New Method. W. G. PALMER (*Proc. Roy. Soc.*, 1923, [*A*], **103**, 444—461).—The rate of oxidation of copper and the rate of reduction of the oxide formed have been studied in the case of a film of copper about 0·001 mm. thick, by continuous determination of the electrical conductivity of the film. It is shown that the oxidation process is not controlled by the rate of diffusion of oxygen into the film. At any definite temperature, the rate of oxidation in the presence of oxygen is proportional to the square root of the pressure of oxygen, up to about 300 mm., and the value of dR/dt is constant, R denoting the resistance of the film at time t. At higher pressures, the rate of oxidation is independent of the pressure. It is assumed that oxygen condenses on the copper as single atoms and that at pressures above 300 mm. the film is completely saturated with atomic oxygen. In the case of the oxidation of copper reduced from oxide at 150°, cuprous oxide first formed begins to be oxidised

to cupric oxide at about 165°. Above 190°, cuprous oxide is again formed, as the rate of oxidation of the latter does not change rapidly with temperature. Metal prepared by reduction at 200° gives rise at all temperatures to cupric oxide only. Results obtained by the oxidation of copper in the presence of hydrogen and of carbon monoxide together with oxygen indicate that the catalytic formation of water or carbon dioxide on the copper increases abnormally the number of copper atoms in a state to be oxidised when brought into contact with an oxygen atom. Initially, the action of the reducing gases is restricted to a slow reduction to metal of oxide already formed, the purely catalytic production of water or carbon dioxide commencing later. It is probable that increased oxidation is most pronounced when the amount of adsorbed reducing gas is comparable with or even exceeds the amount of oxygen on the film. In the case of the reduction of copper oxide by carbon monoxide, the rate of reduction is proportional to the amount of copper in the film and independent of the amount of oxide. When reduction is effected by hydrogen, in general the rate of reduction decreases very rapidly to a low value, although much oxide may be still unreduced. Reduction may be restarted by exhausting and admitting another sample of gas until the pressure is the same as formerly. In this case, the variation of R with t is expressed by the relation $dR/dt=K''R-c'$, where K'' and c' depend on the pressure of hydrogen. c' is the velocity constant of the condensation of water on reduced metal. K'' and c' vary in the same direction when the pressure of hydrogen is altered. J. S. G. T.

The Theory of Ionisation accompanying Combination as the Basis of the Ionic Theory, as deduced from Investigations of the Nature of Non-ionised Acids. A. HANTZSCH (*Z. Elektrochem.*, 1923, **29**, 221—246).—Various experimental data, *e.g.*, the velocity of inversion of sucrose and the rate of decomposition of diazo-acetic esters by undissociated acids, the determination of the strengths of undissociated acids by means of indicators, and the effect of solvents on the degree of acidity, are critically examined in order to elucidate the nature of the process of solution of an electrolyte, more especially in the case of strong undissociated acids. In contradistinction to the ordinary form of the ionic theory which attributes acidity to the presence of ionised hydrogen atoms, and the electrolytic theories proposed by Bjerrum and by Lorenz in which chemical activity is likewise associated with the non-ionised portion of a strong electrolytic solution, the author considers that the ionising effect of water, more especially in the case of the so-called strong acids, is to be explained on purely chemical lines. The author differentiates between true acids containing ionisable hydrogen and having the formula $X{<}\begin{matrix}O\\O\end{matrix}\Big\}H$, which are chemically active, and in their optical properties resemble salts, and pseudo-acids containing hydroxyl hydrogen, having the formula $O{:}X{\cdot}OH$ or $OX{\cdot}OH$. The latter are passive as regards acidity and optically resemble esters. A similar classification is suggested in

the case of salts. Generally, true acids are defined as heteropolar hydrogen compounds containing ionisable, active, combined hydrogen which may be directly substituted by strongly positive metals or complex kations without alteration of structural constitution and without appreciable change of optical properties. Their respective strengths are to be determined by reference to their tendencies towards salt formation in the undissociated state, or by the relative stabilities of their respective salts. They form with water or in aqueous solution hydroxonium salts which are relatively weaker acids owing to their comparative instability compared with the free acid. Pseudo-acids are homöopolar hydrogen compounds containing hydrogen atoms which do not exercise an acid function, and, in the case of oxy-acids, are linked with oxygen in the form of hydroxyl. By addition of water, this hydrogen is transformed either partly or wholly into hydroxonium-ions, and the transformation is accompanied by a change of structural constitution and consequently by a change of optical properties. In aqueous solutions, therefore, both forms of acid react qualitatively in the same manner.

J. S. G. T.

Chemical Reactivity. I. Mechanism of the Formation of Valerolactone. W. H. Garrett and W. C. McC. Lewis (*J. Amer. Chem. Soc.*, 1923, **45**, 1091—1102).—The mechanism of the change hydroxyvaleric acid ⟶ valerolactone has been studied at 25° and 35° in the presence of various concentrations of hydrochloric acid and also in the presence of lithium chloride, potassium chloride, and sucrose, which acted as water displacing agents. It is shown that the reaction is bimolecular, the process actually measured being the rate of effective collision between the suitably activated hydroxyvaleric acid molecules and the hydrogen-ions. A characteristic bimolecular constant is obtained at a given temperature, which is not altered by change in concentration of the catalyst, or by the presence of sucrose, potassium chloride, or lithium chloride in the reaction mixture. This constant involves the activities of the reactants, and also the viscosity of the solution raised to a power characteristic of the hydrogen-ion. This power is not a constant, but varies with the relative size of the individuals in the solution, as determined independently from electrical conductivity measurements. There is a sharp contrast in behaviour between the water of hydration of sucrose, on the one hand, and that of potassium and lithium chlorides, on the other, in respect of the effect on the hydroxyvaleric acid molecule. The water of hydration of sucrose is not available as solvent, whereas that of the neutral salts is available. In none of these cases, however, is hydrogen-ion soluble in water of hydration. The point is considered, but no definite conclusion is drawn. The true critical increment of the reaction is found to be 127,500 cal./mol. of hydroxyvaleric acid transformed. This value is considerably less than the corresponding value obtained on the assumption that the reaction is unimolecular, the difference being 3000 cal./mol. The unimolecular critical increment has, however, no real significance for the process actually measured, which is definitely shown to be bimolecular. J. F. S.

Promotion of Catalytic Reactions. I. SAMUEL MEDSFORTH (T., 1923, **123**, 1452—1469).

Catalysis of Oxygen-Hydrogen Mixtures by means of the Platinum Metals. K. A. HOFMANN (*Ber.*, 1923, **56**, [*B*], 1165—1172; cf. A., 1922, ii, 276, 490).—It is found that the rate of combination of hydrogen and oxygen under the catalytic influence of the metals of the platinum group (except iridium) depends largely on the previous treatment of the catalysts. Previous treatment with hydrogen weakens their catalytic activity, possibly because of the formation of stable hydrides of smaller reducing and electromotive power. Treatment with oxygen increases their activity possibly because of the formation of an unstable oxide which is easily reduced, thus exposing fresh surfaces of active metal to the gas mixture. If, however, this unstable oxide, either by prolonged exposure to the gas, or by anodic polarisation, is converted to the permanent stable form, then a diminution of catalytic activity is observed.

The case of iridium, however, is quite different. The catalytic potential of the iridium surface towards the oxy-hydrogen mixture is almost exactly the mean (+0·42 volt) between that of the hydrogen electrode (zero) and that of iridium saturated with hydrogen towards pure oxygen (+0·82 volt). The iridium catalyst is therefore practically electrically neutral towards this mixture, and previous treatment with either gas has no effect on its catalytic activity. It is also found that the acidity or alkalinity of the medium containing the iridium is without effect on the velocity of reaction between the hydrogen and oxygen. H. H.

Hydrogenation. E. J. LUSH (*J. Soc. Chem. Ind.*, 1923, 42, 219—223T).—Nickel turnings, oxidised electrolytically by making them the anode in the combination Ni|5%Na_2CO_3 solution|Ni, and subsequently reduced in hydrogen, form a very satisfactory catalyst in the hydrogenation of oils. Such freshly reduced catalyst contains sufficient adsorbed hydrogen to effect considerable hardening even in absence of free hydrogen. The surface layer alone is active; but the mass of nickel appears to act as a hydrogen reservoir. The catalyst remains active for long periods, and may be reactivated by extraction with trichloroethylene. The results of some experiments on the hydrogenation of linseed, soja-bean, olive, and cottonseed oils are given. E. E. T.

The Calculation of Atomic Weights. KARL FEHRLE (*Z. Physik*, 1923, **13**, 264—267).—A theoretical paper continuing previous work on ideal and experimental atomic weights (cf. A., 1920, ii, 303, 540). A formula is deduced for the change in experimental atomic weight with atomic number. W. E. G.

An Explanation of the Theory of the Rotation of the Atomic Nucleus. II. HERBERT HENSTOCK (*Chem. News*, 1923, **126**, 321—325; 337—340; cf. this vol., ii, 400).—The application of the author's theory to elements of the groups of the periodic system, taken in order, is discussed and illustrated with diagrams. Par-

ticular interest attaches to the boron hydrides, in which the boron atoms are supposed to form a chain (B_4H_{10}) or a ring (B_6H_{12} and $B_{10}H_{14}$) in which alternative negative and positive atoms are, respectively, ter- and quinque-valent. When ammonia combines with hydrogen chloride, the nucleus of the nitrogen revolves, and it becomes positive in alternative polarity and the hydrogen atoms become negative; the fourth hydrogen unites with the nitrogen by a normal "edge" and with the chlorine by an electrovalence at one of its positive "edges." In hydrazine, the two nitrogen atoms are, respectively, positive and negative, and the molecule is unstable because the positive nitrogen is combined with hydrogen by negative edges. Nitrogen trichloride is unstable because the normally negative nitrogen is united with chlorine along negative edges. The structures of a number of other compounds are discussed on similar lines. E. H. R.

The Phase Relationships in the Bohr Atomic and Molecular Models. M. Born and W. Heisen (*Z. Physik*, 1923, **14**, 44—55).—A theoretical paper in which it is shown that between the movements of the electrons in one and the same atom there must exist phase relationships. Bohr has pointed out this possibility in an explanation of the doublet of orthohelium. It is shown for each atom in the normal condition that the whole system of electronic paths is exactly in phase. Only the relationships in a simple case are studied, where it is possible to follow the reduction of the independent periods. The number of independent quantum phase integrals is not diminished during the process. Some of the principal difficulties of the application of the quantum theory are discussed. W. E. G.

The Application of the Quantum Theory to Atomic Structure. I. Postulates of the Quantum Theory. Niels Bohr (*Z. Physik*, 1923, **13**, 117).—A summary of the postulates of the quantum theory in which it is sought to present a comprehensive theory of atomic structure which will reconcile the formal nature of the quantum theory with the laws of classical electrodynamics. In the application of the quantum theory to a closed atomic system, there are two fundamental postulates. The first postulate requires that any durable change in the motion of an enclosed system shall consist in a complete transference from one stationary condition to another. The second postulate characterises the relation between the energy exchange between an atom and an electromagnetic field, and states that the emission of radiation consists of a series of pure harmonic waves of which the frequency γ is given by the frequence condition $h\nu = E' - E''$, where E' and E'' are the energies of the atom in the initial and final stationary conditions. Both these postulates necessitate a sharp break with the classical laws of electrodynamics. The relationship between the first postulate and these laws is given by the adiabatic principle of Ehrenfest. This requires that the conditions for the stationary state are of such a kind that they fix certain properties of the motion of the system, which do not change during an adiabatic transformation when the

motion is determined with the help of the ordinary electrodynamic laws. It is shown that sharply-defined stationary states must be present in the atom, and this requirement may be designated as the principle of the existence and permanence of the quantum number. The classical laws may be applied to the radiation process with certain limitations determined by the "correspondence" principle. The light quantum hypothesis of Einstein is not suitable for the presentation of a picture of the problems raised by the quantum theory, but the application of the Planck heat radiation law to the emission and absorption processes is more satisfactory. Emphasis is laid on the importance of the adiabatic and correspondence principles for the further extension of the quantum theory of atomic structure. W. E. G.

The Model of the Helium Atom. H. A. KRAMERS (*Z. Physik*, 1923, **13**, 312—341).—A theoretical investigation of the Bohr helium model. The simplest form of this model, in which the electrons move in single quantum orbits about the nucleus as centre, is obtained when the electrons move in the same orbit. This model of the normal condition of the atom gives too high a value for the ionisation potential, and is not in agreement with the spectroscopic experiments of Paschen, or the electron-collision experiments of Franck. In this paper, the model chosen to represent the normal condition of the atom is that where the two electrons move in single quantum orbits in planes which make an angle with one another. It is shown that the energy content of this atom is about 3·9 volts too large and the model in a mechanical sense is unstable. The bearing of these results on the relationship between the classical laws of electrodynamics and the Bohr theory is discussed, and it is concluded that even in the simple model of helium with two identical electrons the mechanical laws have lost their validity, and it is doubtful if the energy function calculated from these laws can be expected to agree with the physical energy derived from spectral terms and from ionisation potentials. W. E. G.

The Normal Paths of the Series Electrons of the Alkalis. A. TH. VAN URK (*Z. Physik*, 1923, **13**, 268—274).—The deviation of the *s*-term quantum number from whole numbers has been ascribed by Schrödinger (*Z. Physik*, 1921, **4**, 347) to the penetration of the inner shells of the atom by the series electrons. This work has been extended, and more accurate calculations have been made of the deviations due to this cause for the alkali metals. They range from +0·74 for sodium to +2·74 for cæsium. Lithium, sodium, and potassium give total quantum numbers for the sharp subordinate series of 2, 3, and 4, respectively; for rubidium it is probably 5, and for cæsium 5 or 6. W. E. G.

The Stability of Atomic Nuclei, the Separation of Isotopes, and the Whole Number Rule. WILLIAM D. HARKINS (*J. Franklin Inst.*, 1923, **195**, 553—573; cf. this vol., ii, 145).—Elements with odd atomic weight and isotopic number but with an even atomic number are rare atomic species. A condition for the

existence of these species is that isotopes with the same isotopic number should occur in at least one of the adjacent elements with lower or higher atomic number. This rule indicates the existence of an isotope of zinc with the isotopic number 7. The elements with odd isotopic numbers are discussed with the aid of a diagram. Attention is directed to the group p_2e, which may be of fundamental importance in atom building, since the formula for any element may be represented as $(p_2e)_M(pe)_N$. A separation of 0·1 unit has been effected in the isotopes of mercury. Photographs are given of the tracks of α-particles through nitrogen gas. The method of separation of gases applied by Hertz to helium and neon, the diffusion of a gas through a moving stream of another gas, is discussed with reference to isotopes, and it is shown that the rate of production of the light fraction decreases logarithmically as the separation in terms of atomic weight increases arithmetically. The theory of the separation by fractionation and the loss in value in collecting finite fractions instead of infinitesimal diffusate fractions is further considered. The time taken to produce a given change in the atomic weight of zinc is 1/28 of that necessary with mercury.

W. E. G.

The Light Elements and the Whole Number Rule. F. W. ASTON (*Nature*, 1923, **111**, 739).—By the use of anode rays of high velocity, it has been shown that the masses of Li^6, Li^7, Gl^9, Na^{23}, Mg^{24}, K^{39}, K^{41}, and Ca^{40} do not diverge from whole numbers in any case as much as 0·1% of the mass measured. Of particular interest is the fact that no difference in mass is detectable between the isobaric atoms Ca^{40} and A^{40}.

A. A. E.

The Electronic Theory of Valency. I. Intramolecular Ionisation. T. MARTIN LOWRY (*Trans. Faraday Soc.*, 1923, 18, 285—295; *Phil. Mag.*, 1923, [vi], **45**, 1105).—The existence of internal ionisation, as suggested by J. J. Thomson (A., 1914, ii, 450) is postulated in the cases of a number of compounds where the charges on the nuclei are not balanced by the enveloping electrons. A "barb" representing an electrovalency, the following constitutional formulæ are suggested for the respective substances: methylethylaniline oxide, $O \leftharpoondown\!\!=\! NMeEtPh$; hydrogen peroxide, $O \leftharpoondown\!\!= O{<}^{H}_{H}$; ozone $O \leftharpoondown\!\!= O{=}O$; hypochlorous acid (non-ionised), $H{-}O{-}Cl$. It is shown by reference to the oxy-acids of chlorine, sulphur, phosphorus, silicon, and various dehydrated acids that stability in oxy-acids depends on the presence of a positive charge on the central atom of the ion, which also increases the strength of the acid. The stability of formic acid depends on the existence of the ion $\overset{-}{O}{-}\overset{+}{C}H{-}\overset{-}{O}$. No significance can now be attached to the conception of "ortho-acids" in which all the oxygen is present as hydroxyl, *e.g.*, $Si(OH)_4$, $P(OH)_5$, $S(OH)_6$, and $Cl(OH)_7$, as the octet theory imposes a limit of four on the primary covalency of all the lighter elements. Acidity originates in the repulsion between a heavy positive nucleus and the light hydrogen nucleus, and a

maximum of strength and stability is reached in acids containing four atoms of oxygen round the central atom of the iron.

J. S. G. T.

The Electron Theory of Valency Applied to Co-ordination Compounds. C. H. SPIERS (*Chemistry and Industry*, 1923, **42**, 534—538).—The author's theory of the structure of co-ordination compounds is similar to that of Lowry (this vol, ii, 313). Lowry's explanation of the reducing action of potassium cobaltocyanide is unsatisfactory; it is due to the complex anion, not to the potassium. His formula for potassium ferrioxalate does not express the different behaviour of the ion and potassium with regard to ionisation. The stability of certain complex ions which exhibit a shortage of electrons may be accounted for on the hypothesis that the innermost pair of electrons, both of the central atom and of the co-ordinated atoms or groups, may be utilised to help the completion of the shell of the central atom (cf. Eastman, A., 1922, ii, 367). This hypothesis reduces the number of complex anions with an incomplete shell to very small dimensions. Thus, out of 32 complex cyanides considered, 26 achieve a complete shell. The utilisation of one inner electron would not appear to be satisfactory; such anions readily gain or lose an electron, for instance, $[Fe(CN)_6]^{---}$ readily becomes $[Fe(CN)_6]^{----}$. The assumption that an atom completes its shell to that of the inert gas immediately following is not always correct. Thus titanium in H_2TiO_3 probably completes to 8 instead of 18, uranium in $[UO_2F_5]K_3$ to 18 instead of 32, and copper in $[CuI_2(S_2O_3)_4](NH_4)_9$ to 32 instead of 18.

The structure of a number of complexes containing ammonia and other nitrogen bases is considered. It is suggested that in ions of the type $[Ni\,en_3]^{++}$ two of the diamine molecules are attached by one nitrogen only to the nickel, thus

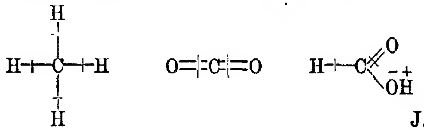
$$\left[\begin{array}{l}CH_2\cdot NH_2 \\ | \\ CH_2\cdot NH_2\end{array}\!\!>Ni<\!\!\begin{array}{l}NH_2\cdot C_2H_4\cdot NH_2 \\ \\ NH_2\cdot C_2H_4\cdot NH_2\end{array}\right]^{++}$$

Similar cases arise where the complex contains a dibasic acid residue. The ease with which ammoniacal silver solutions are reduced is accounted for when it is seen that $[Ag(NH)_2]^+$ has only 16 electrons in its shell even when the two inner electrons are utilised. It readily takes up one electron and decomposes into silver and ammonia. The structure of the oxy-acids of the metals is also discussed. After vanadium these probably complete an 18-electron shell, and this may have something to do with their colour.

E. H. R.

Simplified Method of Writing Electronic Formulæ. ROGER J. WILLIAMS (*J. Amer. Chem. Soc.*, 1923, **45**, 1272—1273).—To obviate the confusion which may arise through the use of the same sign to indicate a single link, a negative charge in ionisation and a negative polarity in organic compounds, the author proposes to cross the valency links at the end where there is a positive polarity, the other end of the link obviously representing a negative polarity without any further sign, ionisation being represented as before,

thus avoiding all confusion. Where the polarity is unknown or where there is no desire to represent it, the links are drawn in the usual manner. Examples of the method given are :



J. F. S.

Unification of the Laws of Chemical Combination. E. PUXEDDU (*Gazzetta*, 1923, **53**, i, 204—209; cf. A., 1919, ii, 460).—According to the views held by the author, the laws of constant proportions, of multiple proportions, of equivalents, of Gay-Lussac on gaseous compounds, etc., represent nothing but different aspects of a single principle. Balareff's work (A., 1918, ii, 15) is discussed further, and it is pointed out that this author's enunciation of the law of multiple proportions is not an improvement on the older form and is not in accord with the meaning of Dalton's principle. In view of the formulæ of compounds of the protein group, characterisation of the ratios of the weights in which different elements unite with one another as simple is absurd. T. H. P.

Baeyer Memorial Lecture. WILLIAM HENRY PERKIN (T., 1923, **123**, 1520—1546).—A lecture delivered before the Chemical Society on May 10th, 1923.

Inorganic Chemistry.

Active Hydrogen : Its Preparation from Metallic Hydrides. Y. VENKATARAMAIAH (*Proc. Sci. Assoc. Vizianagram*, 1922, Dec. 6).—Hydrogen obtained by the decomposition of sodium, potassium, or calcium hydride yields with sulphur traces of hydrogen sulphide. A. A. E.

Precision Measurement of the Composition of the Constant Boiling Mixture of Hydrogen Chloride and Water. C. W. FOULK and MARION HOLLINGSWORTH (*J. Amer. Chem. Soc.*, 1923, **45**, 1220—1228).—The composition of the constant boiling mixture of hydrogen chloride and water has been accurately determined by weighing the silver chloride formed. The following results of the composition of the liquid obtained at various pressures are recorded: 770 mm., 20·197%; 760 mm., 20·221%; 750 mm., 20·245%; 740 mm., 20·269%, and 730 mm., 20·293%. It is shown that the rate of distillation affects the composition to a small extent. The present results are compared with those published by Hulett and Bonner (A., 1909, ii, 342), Morey (A., 1912, ii, 986), and Hendrixson (A., 1915, ii, 797), who give for 750 mm. 20·258%, 20·252%, and

20·253%, respectively, against 20·245% obtained in the present experiments by rapid distillation. J. F. S.

Anhydrous Perchloric Acid. D. VORLÄNDER and ERICH KAASCHT (*Ber.*, 1923, **56**, [*B*], 1162—1164).—The dark reddish-brown colour of the solution obtained by the action of strong sulphuric acid on potassium chlorate is not due entirely to chlorine dioxide, for this substance in solution is at most red or dark yellow in colour. The authors ascribe the dark brown colour to an unstable compound of chlorine dioxide and perchloric acid. Anhydrous perchloric acid saturated with chlorine dioxide at −15° yields a brown, crystalline slurry which melts below 0°, decomposes in ice-water, and is soluble in chloroform to a yellow solution. Neither bromine nor sulphuryl chloride acts on perchloric acid. Dry hydrogen bromide at −15° and hydrogen chloride at −70° are similarly without action. Potassium perchlorate, boric acid, and arsenic can be crystallised from 70% perchloric acid. Attempts to prepare the chloride of perchloric acid by the action of phosphorus pentachloride were unsuccessful, the distilled product always containing large amounts of phosphorus. H. H.

The Ageing of Thiosulphate Solutions. E. ABEL (*Ber.*, 1923, **56**, [*B*], 1076—1079; cf. Hahn and Windisch, A., 1922, ii, 873).—The ageing of volumetric thiosulphate solutions consists in a gradual diminution of activity due to the combined action of atmospheric oxygen and carbon dioxide which is opposed by the increasing alkalinity of the solution followed by a cessation of the change, so that aged solutions are practically constant in their activity under uniform working conditions. It appears to the author that the changes are probably due to the catalytic action of traces of copper. The course of the action is expressed by the schemes: $2Cu^{\cdot\cdot}+2S_2O_3''=2Cu^{\cdot}+S_4O_6''$; $2Cu^{\cdot}+\frac{1}{2}O_2\longrightarrow 2Cu^{\cdot\cdot}+O''$; $O''+2H^{\cdot}\longrightarrow H_2O$. The function of the carbon dioxide is to form carbonic acid and thus provide the necessary hydrogen-ions, since otherwise the catalyst would be precipitated and rendered practically inactive by the hydroxyl-ions. Stabilisation of the solutions by addition of alkali (or corresponding compounds which neutralise acids and precipitate copper) is thus satisfactorily explained. The automatic stabilisation of the solutions by ageing is due, not only to consumption of the dissolved carbon dioxide, but also to loss of catalytic activity of the copper.

Attention is directed to the readiness with which traces of copper pass into water which is distilled from copper vessels. It is recommended that the water used for thiosulphate solutions should be distilled in glass vessels, and that due care should be taken to prevent ingress of copper from the laboratory air. Solutions prepared with these precautions maintain their concentration excellently. H. W.

The Viscosity and Molecular Dimensions of Hydrogen Selenide. C. J. SMITH (*Trans. Faraday Soc.*, 1923, **18**, 302—307).—The value of the viscosity of hydrogen selenide at 20·0° is found to be $1·68\times10^{-4}$ C.G.S. unit. The value of Sutherland's

constant, C, for the gas, deduced from the empirical relation C/T_B=a constant, for gases of similar constitution and occupying corresponding places in the periodic table, where T_B is the boiling point of the gas on the absolute scale, is 365. The value of the mean collision area of the molecule of hydrogen selenide deduced from these results is $0{\cdot}86\times10^{-15}$ sq. cm. The series of gases, hydrogen bromide, hydrogen selenide, and arsine have a central atom resembling an atom of krypton, and the increase in the value of the mean collision area of the molecules of these gases on passing from krypton to arsine is to be attributed to the hydrogen nuclei attached to the central atom. As the number of hydrogen atoms in the molecule increases, the distance of each hydrogen nucleus from the centre of the molecule increases at an increasing rate.

J. S. G. T.

Solubilities of certain Metallic Chlorides in Selenium Oxychloride. CLARENCE R. WISE (*J. Amer. Chem. Soc.*, 1923, **45**, 1233—1237).—The solubility of a number of anhydrous metallic chlorides in anhydrous selenium oxychloride has been determined. The following solubilities at 25° are recorded: lithium chloride, 3·21%; sodium chloride, 0·57%; potassium chloride, 2·89%; rubidium chloride, 3·56%; cæsium chloride, 3·83%; magnesium chloride, 4·96%; calcium chloride, 6·11%; strontium chloride, 5·17%; barium chloride, 3·95%; zinc chloride, 1·10%; cadmium chloride, 0·15%; mercuric chloride, 0·89%; titanium tetrachloride, 0·75%; stannic chloride, 13·73%; arsenic trichloride is miscible in all proportions; antimony pentachloride, 38·64%; manganous chloride, 0·16%; ferric chloride, 23·40%; nickel chloride, 0·15%; and cobalt chloride, 0·17%. Cupric chloride, silver chloride, and lead chloride are less soluble than 0·1%. The solubility is given in terms of 100 g. of saturated solution. The presence of a trace of water makes a great difference in the solubility. This is shown in the case of the solubility of barium chloride, where the following values are obtained for selenium oxychloride containing the number of molecules of water stated per molecule of oxychloride: anhydrous, 3·95%, $\frac{1}{16}H_2O$, 3·86; $\frac{1}{8}H_2O$, 3·37; $\frac{1}{4}H_2O$, 2·32; $\frac{1}{2}H_2O$, 1·40; $1H_2O$, 0·45. The following double compounds have been isolated during the present work: $TiCl_4,2SeOCl_2$; $SnCl_4,2SeOCl_2$; $SbCl_5,2SeOCl_2$; $FeCl_3,2SeOCl_2$; $KCl,SeOCl_2$; $RbCl,SeOCl_2$; $CaCl_2,3SeOCl_2$; $MgCl_2,3SeOCl_2$. Cæsium chloride forms a yellow, gelatinous mass which is too indefinite for analysis. None of the other chlorides investigated give double compounds. J. F. S.

Spatial Distribution of the Valencies of the Tervalent Nitrogen Atom in Connexion with the General Theory of Asymmetry of Molecules and of Optical Activity. A. E. USPENSKI (*J. Russ. Phys. Chem. Soc.*, 1920, **51**, 288—295).—The question of the spatial distribution of the valency directions of tervalent nitrogen is discussed, and shown to be definitely settled in the cases of singly and doubly linked nitrogen atoms, but not in the case of nitrogen atoms contained in heterocyclic rings.

R. T.

Peroxidation of Nitric Oxide. II. E. BRINER and G. MALET (*J. Chim. Phys.*, 1923, 20, 173—200; cf. A., 1922, ii, 563).—With the object of clearing up the different views held with regard to the mechanism of the oxidation of nitric oxide, the authors have investigated the range of oxidation below 50% by the method of absorption of the nitrous gases. The retardation of the commencement of the reaction, which is essential if the necessary observations are to be made, has been achieved by operating with very dilute mixtures of nitric oxide and oxygen and the losses which always accompany the absorption of dilute mixtures of nitrous gases have been evaluated by means of correction curves. The absorption curves show that the oxidation takes place continuously and in a single stage, with the formation of nitrogen dioxide. Nitrous anhydride which is found in the products of the reaction is the result of a secondary reaction. When the results are considered kinetically, they show that the reaction is of the third order and must be expressed $2NO+O_2=2NO_2$ (N_2O_4). Calculations connected with this process ought therefore to be made with equations suited for reactions of the third order, except in those cases where the excess of oxygen is sufficiently great (at least twenty times the theoretical quantity), and here it is correct to use the simpler equations of second order reactions. This case is realised in the practical problem of the recovery of nitrous gases obtained in the fixation of nitrogen by the electric arc processes. Using these equations, the authors have calculated the absolute velocity constants from the absolute concentrations and the relative velocity constants from the percentage composition. The equation $K=1/t\,.\,x/(b-x)$, where K has the value 0·032 for ordinary temperature and pressure, may be employed for calculating values of technical significance such as the relationship between the amount of oxidation and the temperature, the time necessary to ensure 50% oxidation, and the volume of the chambers necessary to furnish any given amount of oxidation. J. F. S.

Physico-chemical Investigations of the Properties and Electrolysis of Solutions of Alkali Azides. E. BRINER and P. WINKLER (*Helv. Chim. Acta*, 1923, 6, 429—435; *J. Chim. Phys.*, 1923, 20, 201—216).—When an alkaline solution of azoimide is electrolysed pure nitrogen is liberated at the anode, but the quantity obtained is not theoretical, and Peratoner and Oddo (A., 1896, ii, 245) attribute the deficiency to formation of nitric acid. If the formation of nitric oxide could be proved by the interaction of anodic nitrogen and nascent oxygen, this would furnish an argument in favour of the atomic fixation of nitrogen, the atomic nitrogen coming from the decomposition of the N_3-ion. The formation of nitric acid by the electrolysis of an alkaline solution of an azide has been confirmed. Such a solution evolves much free oxygen with the nitrogen, but the amount of nitric acid formed is very minute. When a neutral azide solution was electrolysed and a stream of oxygen was led into the anodic nitrogen, no nitric oxide was found in the gases, and the amount of nitric acid in

solution was even less than from the alkaline solution. When ozone was used with the oxygen, the nitric acid reaction in the solution became very distinct. When hydrogen was led into the anode chamber very minute quantities of ammonia were formed, but when an aluminium anode was used, causing the formation of nascent hydrogen by solution of the metal in the alkaline liquid, ammonia was formed freely. Only one-third of the nitrogen of the azide is converted into ammonia, the other two-thirds escaping as nitrogen. It may be taken, therefore, that the azoic group decomposes according to the equation $N_3=N_2+N$, giving rise to an atom of nascent nitrogen. E. H. R.

Certain Physical Properties of Arsenic Trioxide in Water Solution. ERNEST ANDERSON and LEROY G. STOREY (*J. Amer. Chem. Soc.*, 1923, **45**, 1102—1105).—The density, refractive index, and hydrogen-ion concentration of solutions of arsenious oxide of various concentrations in water have been determined, and preliminary experiments are described on the determination of the amount of the oxide converted into arsenious acid. The following values of d_{25}^{25} are recorded for solutions containing the number of grams stated per litre of solution. 1·796 g., 1·0014; 3·212 g., 1·0025; 5·060 g., 1·0039; 6·425 g., 1·0050; 7·184 g., 1·0057; 8·561 g., 1·0068; 10·13 g., 1·0080; 11·35 g., 1·0089; 12·85 g., 1·0102, and 14·368 g., 1·0013. The density composition curve is a straight line, represented by the equation $W=-1288{\cdot}36+1288{\cdot}39d$, where d is the density and W the number of grams of arsenious oxide per litre of solution. The refractive index, measured by means of an immersion refractometer, also varies in a linear manner with the composition and is represented by $W=-10062{\cdot}7+7550r$, where r is the refractive index at 22°. The solubility of arsenious oxide in water has been determined at 0°, 15°, 25°, 39·8°, 48·2°, 62°, 75°, and 98·5°, and the following values in g. per 100 c.c. of water have been obtained: 0°, 1·21; 15°, 1·66; 25°, 2·05; 39·8°, 2·93; 48·2°, 3·43; 62°, 4·45; 75°, 5·62, and 98·2°, 8·18. The solubility is represented by the equation $W=1{\cdot}21+0{\cdot}021t+0{\cdot}000505t^2$. Arsenious oxide is least soluble in 3·2*N*-hydrochloric acid (cf. Wood, T., 1908, **93**, 413). Attempts to measure the hydrogen-ion concentration of solutions of arsenious oxide by *E.M.F.* measurements were unsuccessful, owing in all probability to a reduction of the oxide (cf. Gladstone and Tribe, T., 1878, **33**, 306), but using the Sörensen indicator method the value $P_H=6{\cdot}6$ was obtained. The molecular weight of arsenious oxide determined in water solution by the ebullioscopic method is 92·5 and by the cryoscopic method 99·17, which appears to indicate that at 0° some form of arsenious oxide is present, possibly $HAsO_2$. J. F. S.

Silicon Hydrides. XV. Trisilane and Chloroform. ALFRED STOCK and PAUL STIEBELER (*Ber.*, 1923, **56**, [*B*], 1087—1091).—The violently explosive action between the silanes and carbon tetrachloride or chloroform (cf. Moissan and Smiles, A., 1902, ii, 308; Stock and Somieski, A., 1916, ii, 319) is only observed in the presence of oxygen, mere traces of which are sufficient to

induce the change. The *rôle* of the oxygen has not been elucidated, but its activity does not appear to depend on the initial formation of water.

The reaction between trisilane and chloroform in the molecular ratio 1 : 4·3 has been investigated at 50° in the presence of aluminium chloride (in the absence of the latter, the change proceeds too violently or not at all). Reaction occurs mainly in accordance with the equations: $Si_3H_8+4CHCl_3=Si_3H_4Cl_4+4CH_2Cl_2$ and $Si_3H_8+5CHCl_3=Si_3H_3Cl_5+5CH_2Cl_2$. Small quantities of methane and methyl chloride are also produced, whilst a little chloroform remains unattacked. The chlorotrisilanes are mixtures of isomerides. H. W.

Influence of certain Fluxes on the Transformations of Quartz. N. PARRAVANO and C. ROSSELLI DEL TURCO (*Gazzetta*, 1923, **53**, i, 249—257).—The authors have investigated the influence of small proportions of ferric oxide, phosphoric anhydride, boric anhydride, lime, and tungstic oxide on the character of the refractory obtained from quartzite. [Cf. *J.S.C.I.*, 1923, July.]

T. H. P.

A Critical Search for a Heavier Constituent of the Atmosphere by Means of the Mass-spectrograph. F. W. ASTON (*Proc. Roy. Soc.*, 1923, [*A*], **103**, 462—469).—From the results of analysis by the mass-spectrograph of liquid oxygen residues derived from more than 400 tons of air, the author concludes that a gaseous inert element heavier than xenon is certainly not present in air to the extent of 1 part in 10^{15} parts and probably not to the extent of 1 part in 2×10^{16} parts of air by volume. The results do not support Thomson's suggestion of the presence of molecular krypton and xenon in the air (A., 1922, ii, 565). The origin of a faint band corresponding with mass 260 appears to be connected with the presence of xenon, but the connexion is not necessarily a direct one. A faint band corresponding with mass 260 is attributable to a complex molecule of mercury with a multiple charge.

J. S. G. T.

New [Crystalline] Forms of Perchlorates. D. VORLÄNDER and ERICH KAASCHT (*Ber.*, 1923, **56**, [*B*], 1157—1162).—Enantiotropic forms of the alkali perchlorates are described and their transition points determined by microscopic, thermometric, and dilatometric methods. When, for instance, potassium perchlorate is heated to a temperature well below its decomposition point, it changes to a regular, optically isotropic form, thus:

$$\underset{\text{rhombic}}{\beta\text{-}KClO_4} \underset{293^\circ}{\overset{299\cdot5^\circ}{\rightleftharpoons}} \underset{\text{regular}}{\alpha\text{-}KClO_4}.$$

It is found that the transition temperatures of the dimorphous forms of the alkali perchlorates fall, although not in a regular manner, with increasing atomic weight of the metal: $NaClO_4$, 308°; $KClO_4$, 299—300°; $RbClO_4$, 279°; $CsClO_4$, 219°; NH_4ClO_4, 240°. The transition point of the ammonium salt lies between

those of the rubidium and cæsium salts, thus coming into line with the other physical properties of ammonium salts.

Thallium perchlorate has a transition point at 266°, and the anhydrous silver salt at 155—159°, although the latter begins to decompose at the transition point. Silver perchlorate, however, appears to change from a weakly to a strongly doubly refracting form at a temperature between 102° and 110°. The anhydrous perchlorates of lithium, magnesium, calcium, and strontium exist only in one form, this being another example of the similarity between lithium and the metals of the alkaline earths.

Barium perchlorate exists in two forms, which are, however, both optically anisotropic, and are transformed one into the other at 284°. Tetramethylammonium perchlorate exists in rhombic and regular forms, transition point about 350°. Phenyltrimethylammonium perchlorate melts and decomposes before reaching a transition point. Potassium permanganate could not be shown to exist in two forms. H. H.

The Freezing-point Curve for Mixtures of Potassium Nitrate and Sodium Nitrate. HENRY VINCENT AIRD BRISCOE and WALTER MATTHEW MADGIN (T., 1923, **123**, 1608—1618).

The Normal and Acid Sulphates of Sodium. P. PASCAL and ERO (*Mém. Poudres*, 1923, 20, 1—16).—The system Na_2SO_4–H_2SO_4–H_2O was studied. The following salts are in equilibrium with the liquid phase at various concentrations and temperatures: Na_2SO_4; $Na_2SO_4,7H_2O$; $Na_2SO_4,10H_2O$; $Na_2SO_4,NaHSO_4$; $NaHSO_4$; $NaHSO_4,H_2O$; $NaHSO_4,H_2SO_4$; $NaHSO_4,H_2SO_4,1{\cdot}5H_2O$; $2NaHSO_4,Na_2SO_4$. Below 120°, the solubility of sodium sulphate was determined at different temperatures in sulphuric acid of different concentrations, and the liquid and solid phases were analysed when equilibrium had been attained. Further points on the diagrams were obtained by observing the temperatures at which solid began to be deposited from solutions of known composition. Finally, the form of the isothermals was definitely fixed by thermal analysis. Sodium hydrogen sulphate melts at 185° and its monohydrate at 112°. The salts $NaHSO_4,H_2SO_4$ and $NaHSO_4,H_2SO_4,1{\cdot}5H_2O$ have no definite melting points. The former is liquid above 107·5°, and the latter at 131°. The salt $NaHSO_4,Na_2SO_4$ decomposes at 174°, and partly liquefies with deposition of the neutral anhydrous sulphate. Isothermals with 25° intervals are given for this system on a triangular diagram, and a further diagram gives the regions of stability of the various salts enumerated above. Solutions of pure sodium hydrogen sulphate in water can only deposit the normal decahydrate above 4°, whilst at room temperature they can only give the salt $NaHSO_4,Na_2SO_4$. In order to obtain crystals of the pure hydrogen sulphate it is essential to have a considerable amount of acid in the solution. Certain deposition of the salt $NaHSO_4$ can only be obtained from 65% sulphuric acid. Compounds of sodium hydrogen sulphate and sulphuric acid are only deposited from sulphuric acid solutions of above 80%. It is impossible to obtain the salt

$NaHSO_4,Na_2SO_4$ from aqueous solution. The processes for obtaining sulphuric acid by the hydrolysis of sodium hydrogen sulphate are reviewed from the point of view of the diagrams obtained. The whole acidity of the sodium hydrogen sulphate can be obtained as sulphuric acid by depositing the decahydrate from comparatively dilute solution with the aid of refrigeration, or the intermediate salt may be deposited from more concentrated solutions without recourse to refrigeration. In the latter case, the whole of the acidity is not recovered as sulphuric acid. The two methods are analysed with the aid of a further triangular diagram. A diagram of the melting points of mixtures of normal sulphate with sulphuric acid is given. H. C. R.

Preparation of Sodium Metaphosphate at a Low Temperature. PAUL PASCAL (*Compt. rend.*, 1923, **176**, 1398—1400).—When prepared by the action of sodium ethoxide on ethyl metaphosphate in presence of ether at 35—40°, sodium metaphosphate exhibits properties which differ from those of the polymeride usually described as metaphosphate. The substance obtained in the reaction has a molecular weight which, in dilute solution, tends to the limiting value 51, corresponding with the complete ionic dissociation of $NaPO_3$. The constitution of the salt undergoes no change on being heated at temperatures ranging up to 800°. It is pointed out that as ethyl metaphosphate is a hexametaphosphate, $(EtPO_3)_6$, the reaction involves the breaking-down of a complex.
H. J. E.

The Behaviour of Calcium Oxide towards Water. V. KOHLSCHÜTTER and W. FEITKNECHT (*Helv. Chim. Acta*, 1923, **6**, 337—369).—In a previous paper (Kohlschütter and Walther, A., 1919, ii, 342), it was shown that the slaking properties of lime depend to a great extent on the source of the lime, whether it be made from calcium carbonate, oxalate, or hydroxide. These differences are now shown to extend to other properties of lime, so far as these can be measured quantitatively; these include the "looseness" of the powder; the rate of slaking in moist air, when the first mol. of water is absorbed at a linear rate, and a further 0·5 mol. at a gradually decreasing rate; and the volume change when slaking is completed. Further, the rate of slaking in much water, measured calorimetrically by the rate of heat-development, showed similar differences. Samples of lime made from amorphous oxalate and from nitrate, which were exceptionally dense, slaked very slowly. Calcium chloride and sodium chloride in the slaking water accelerate the rate of slaking, whilst sodium acetate, calcium hydroxide, calcium sulphate, and particularly sodium hydroxide have a retarding action which is most marked at the later stages. The influence of the electrolyte increases with its concentration. Milk of lime prepared from quicklime has a greater viscosity and settles more slowly than that prepared from lime first slaked by water vapour.

The above and a large number of other similar observations lead to the conclusion that the characteristic properties of lime are due to the fact that it is a disperse substance formed by topo-

chemical decomposition of a crystalline substance. The primary particles of the product are probably crystalline, but these, owing to the duration of the heating, aggregate to form secondary particles. The formation of hydroxide is also a topochemical change, consequently the character of the hydroxide depends as much as that of the oxide on the source from which it has been obtained. [See also *J.S.C.I.*, 1923, July.] E. H. R.

System Calcium Oxide–Carbon Dioxide. F. HASTINGS SMYTH and LEASON H. ADAMS (*J. Amer. Chem. Soc.*, 1923, 45, 1167—1184).—An apparatus is described by means of which the pressure–temperature relations in the system calcium oxide–carbon dioxide can be investigated up to 1390° and 1000 megabars pressure. Using this apparatus, equilibrium pressures have been determined which, together with the previously published data obtained by Johnston (A., 1910, ii, 831), define the system experimentally from 587° to 1339° and from 1 mm. to 779,000 mm. pressure. An equation has been deduced which fits the pressure–temperature curve at all points within the limits of experimental error up to the eutectic point for the system calcium carbonate–carbon dioxide. This equation has the form $\log p = -11355/T - 53{\cdot}88 \log T + 29{\cdot}119$. The melting point of calcium carbonate containing only 0·38% of calcium oxide is found to be 1339° at 779,000 mm. pressure. This value probably lies very near to the melting point of pure calcium carbonate. The eutectic between calcium carbonate and calcium oxide has been experimentally determined and found to lie at 1240±1° at 30,000 mm.±300 mm. The composition as judged from microscopic examination is about 50% calcium carbonate and 50% calcium oxide. The heat change, ΔH, for the reaction $CaCO_3 \longrightarrow CaO + CO_2$ is given by $\Delta H = 51990 - 10{\cdot}71T$, and the values 48800, 45850, 42640, 40500, 38360, and 36210 cal. are calculated for 25°, 300°, 600°, 800°, 1000°, and 1200°, respectively. The free energy change, $-\Delta F$, of the reaction is given by $-\Delta F = 120{\cdot}136T - 24{\cdot}670T \log T - 51991$ if the final pressure is one atmosphere, and $-\Delta F = 120{\cdot}149T - 24{\cdot}670T \log T - 51991$ if the final pressure is one megabar. It has been shown both from thermodynamic and experimental evidence that only one crystalline form of calcium carbonate exists within the temperature range investigated. J. F. S.

Separation of Isotopes of Zinc. A. C. EGERTON and W. B. LEE (*Proc. Roy. Soc.*, 1923, [*A*], **103**, 499—515).—Two sets of distillations of pure zinc were carried out in high vacuum under conditions to obtain a slightly different concentration of the isotopes in the final residue of the last distillate. For the determination of densities, the metal was cast in a vacuum and seeded with about 1 mg. of a particular kind of zinc. The first set of distillations gave a residue of slightly increased density, but the distillate was of the same density as the original zinc. The second set of distillations, carried out under improved conditions yielded a residue of increased density (about 1 part in 3,700 parts), and a distillate of decreased density (about 1 part in 3,600 parts). The density

of ordinary zinc at 16·3°, determined from seven samples of the metal prepared as described, was found to be 7·1400±0·0006. The possibility of attributing the difference of densities to flaws, allotropes, different physical conditions, and impurities is discussed and shown to be improbable. The degree of separation obtained agrees with Dempster's observations of isotopes of weights 64—70, but is less than half what might be found for equal parts of an isotope of mass 64, and of isotopes 66, 68, and 70. J. S. G. T.

Lithopone. I. The Mechanism of the Chemical Reactions occurring in the Blackening of Zinc Sulphide on Exposure to Light. E. MAAS and R. KEMPF (*Z. angew. Chem.*, 1923, **36**, 293—297).—The blackening of lithopone on exposure to light has been shown to be due to the calcined zinc sulphide it contains. The authors examine the various hypotheses put forward to explain the blackening of the latter compound, and discuss them in the light of their own and other experiments. They conclude that the phenomenon is due to the zinc sulphide forming zinc disulphide and finely divided metallic zinc on the surface of the mass. The mechanism of the process, they consider, is the same as that referred by Fajans to the action of light on silver bromide (*Chem. Zeit.*, 1922, **46**, 910). The ultra-violet rays in the light cause the transference of an electron from a negatively charged sulphur-ion on the surface of the crystal lattice of zinc sulphide to a neighbouring positively charged zinc-ion, whereby free uncharged atoms of zinc and sulphur are formed. The zinc appears as finely divided metal, the sulphur atom combines with neighbouring zinc- and sulphur-ions to form zinc disulphide. Amorphous freshly precipitated zinc sulphide not possessing a lattice structure is not sensitive to light; neither is zinc sulphide which has been ground in a mortar, since here the lattice arrangement has been disturbed. Blackened lithopone brightens in the dark owing to oxidation of the metallic zinc, for it remains black if no oxygen is present. T. S. W.

The Vapour Pressure of Lead. I. A. C. EGERTON (*Proc. Roy. Soc.*, 1923, [*A*], **103**, 469—486).—The vapour pressure of lead has been determined for the range of temperatures 837—1045° (abs.) by determining the rate of effusion of the vapour at high vacuum through an orifice of known area. A difference of 2% in the vapour pressure of lead and of uranium lead was observed at 700°, corresponding with no energy term at absolute zero, and in agreement with the 1·5 log M law for the chemical constant (*Phil. Mag.*, 1919, **38**, 178). At temperature T between 600° and 1200° (abs.) the vapour pressure, p, is expressed by the relation $\log p = 7{\cdot}908 - 9923/T$. The value of the chemical constant of ordinary lead, deduced from what are considered to be the most accurate measurements of vapour pressure, is 1·8±0·2, agreeing with the theoretical value 1·853 calculated from $1{\cdot}5 \log M - C_0$, where M=the molecular weight (207·2) and C_0=1·622 (A., 1920, ii, 84). The calculated value of the heat of vaporisation of lead at absolute zero is 47,000±1000 calories. The latent heat of

vaporisation of the molten metal varies very little with temperature up to 1200° (abs.), and is equal approximately to 45,350 cal. A lowering of vapour pressure occurs when lead is heated in a vacuum for long periods under the conditions of the present experiments.
J. S. G. T.

Univalent Thallium in certain Sulphito-salts. G. CANNERI (*Gazzetta*, 1923, **53**, i, 182—185).—A number of analogous double sulphites of thallium and bivalent metals of the form $X^{II}(SO_3)_2Tl_2$ have been prepared by passing sulphur dioxide into an aqueous suspension of the hydroxide of the bivalent metal until this is completely dissolved and adding concentrated thallous carbonate solution. In these compounds the bivalent metal functions as co-ordinant and the thallium is situated outside the co-ordinating nucleus. The compounds form microcrystalline powders: *zinc*, pink; *cadmium*, pink; *ferrous*, brick red; *manganous*, white; *nickel*, yellow; *cobalt*, pink.
T. H. P.

The Action of Sodium Hyposulphite on Cupric Chloride in Aqueous Solution. JAMES BRIERLEY FIRTH and JOHN HIGSON (T., 1923, **123**, 1515—1519).

Chlorites of Copper and other Metals. GIORGIO RENATO LEVI and C. CIPOLLONE (*Gazzetta*, 1923, **53**, i, 200—203; cf. this vol., ii, 421).—*Cupric chlorite*, $Cu(ClO_2)_2$, forms a yellowish-brown precipitate, undergoes rapid change even in a closed vessel, and explodes violently on percussion. *Basic cupric chlorite*,

$$Cu(ClO_2)_2,3Cu(OH)_2,$$

does not explode when struck. *Potassium cupric chlorite*, $Cu(ClO_2)_2,2KClO_2,2H_2O$, obtained as a green, crystalline precipitate, explodes on percussion, and forms dark brown concentrated, and green dilute, aqueous solutions. The *double* salt, $CuCl_2,KClO_2$, is a reddish-brown, stable compound and does not explode on percussion. The *double* salt, $CuCl_2,NH_4ClO_2$, is similar to the preceding salt. *Rubidium chlorite*, $RbClO_2$; the *double* salt, $CuCl_2,RbClO_2$; *cæsium chlorite*, $CsClO_2$, which is hygroscopic; the *double* salt, $CuCl_2,CsClO_2$; *cadmium chlorite*, $Cd(ClO_2)_2,2H_2O$, which is very stable and is not exploded by percussion; and *zinc chlorite*, $Zn(ClO_2)_2,2H_2O$, which is greenish-yellow and does not explode when struck, have also been prepared.
T. H. P.

Action of Solutions of Alkali Hydroxides on Copper Oxide and on Copper, and the Existence of Salts of Cupric Acid. H. J. M. CREIGHTON (*J. Amer. Chem. Soc.*, 1923, **45**, 1237—1243).—Blue solutions containing copper have been prepared by dissolving cupric hydroxide in concentrated alkali hydroxide, by digesting copper oxide with concentrated solutions of alkali hydroxide at 80—90°, and by electrolysing concentrated solutions of alkali hydroxide between copper electrodes with a high current density at 80—90°. The blue solutions obtained by these methods are identical in their behaviour. The blue substance which is formed when copper oxide is added to molten potassium hydroxide may be the same as the blue component of these solutions. None of

the blue solutions exhibit the characteristic properties of colloidal solutions, particularly those of the solutions of colloidal hydroxide prepared by Ley (A., 1905, ii, 524). Evidence is put forward which indicates that the blue colour of the solutions is due to the presence of an alkali salt of cupric acid. The formation of the salt by the second method can be represented $CuO+2OH' \rightarrow CuO_2''+H_2O$, and that by the third method by $Cu+2\oplus \rightarrow Cu^{\cdot\cdot}+4OH' \rightarrow CuO_2''+2H_2O$. The solubility of the alkali cuprates in alkali hydroxides, although quite low, increases rapidly with the concentration of the hydroxide. The potassium salt is apparently more soluble than the sodium salt. J. F. S.

Revision of the Atomic Weight of Mercury. O. Hönigschmid, L. Birckenbach, and M. Steinheil (*Ber.*, 1923, **56**, [*B*], 1212—1219).—Mercury was purified by shaking with aqueous mercurous nitrate, then dropping in a fine stream through 1 metre of 5% nitric acid, followed by three distillations in a vacuum, rejecting all but the middle fraction each time. The pure mercury was converted into the chloride or bromide by heating in a quartz vessel in a current of the dry halogen. The mercuric halide thus obtained was twice sublimed and once melted, also in a quartz vessel. Weighed quantities of the halides were reduced in ammoniacal solution by means of halogen-free hydrazine, and the resulting ammonium halide was titrated nephelometrically with silver nitrate. Twelve determinations of the ratio $HgCl_2:2Ag$ gave $Hg=200{\cdot}61\pm0{\cdot}006$ ($Ag=107{\cdot}88$; $Cl=35{\cdot}457$). Eight determinations of the ratio $HgBr_2:2Ag$ gave $Hg=200{\cdot}61\pm0{\cdot}00$ ($Br=79{\cdot}916$), mean $Hg=200{\cdot}61$ (see following abstract). H. H.

The Atomic Weights of Isotopes of Mercury. O. Hönigschmid and L. Birckenbach (*Ber.*, 1923, **56**, [*B*], 1219—1221; cf. preceding abstract and A., 1922, ii, 295).—Pure mercury was distilled at a low temperature in a high vacuum, and the atomic weights of the extreme fractions were determined by the method described in the preceding abstract. Light fraction, density 0·999824 (ordinary mercury=1·000000), atomic weight=$200{\cdot}564\pm0{\cdot}006$; dense fraction, density 1·000164, atomic weight=$200{\cdot}632\pm0{\cdot}007$. H. H.

The Arrangement of the Atoms in Crystals of Cinnabar. Ch. Mauguin (*Compt. rend.*, 1923, **176**, 1483—1486).—The reflection of *X*-rays from the crystal faces was observed and a theoretical consideration of the results obtained shows that no definite conclusion can be drawn until a more exact measure of intensities is available and also some knowledge of the laws of diffraction of *X*-rays by mercury and sulphur atoms. H. J. E.

Hydrates and Hydrogels. II. An Aluminium Hydroxide Gel of the Formula $Al(OH)_3$. Richard Willstätter and Heinrich Kraut (*Ber.*, 1923, **56**, [*B*], 1117—1121; cf. this vol., ii, 167).—The authors have continued the work described in their previous communication on the subject and now describe a method

of preparation of an improved form of hydrogel *C*. The essential condition for the formation of the new variety is the precipitation of an aluminium sulphate solution with a very slight excess of ammonia at 60°. The solution must not be allowed to become more than weakly alkaline, as high concentration of hydroxyl-ion is fatal to success. The gel was obtained free from sulphate as a flocculent, somewhat plastic mass with a faint yellow tinge. It is amphoteric in character, and in contrast with acidic preparations of the gel, adheres strongly to glass surfaces.

It is very easily soluble in acids and in alkalis. In 1% hydrochloric acid, in which the *D*-form is insoluble, it dissolves completely in five minutes on warming, giving a clear solution showing no Tyndall effect. It dissolves immediately in warm 15% hydrochloric acid, and in half an hour in 35% acid. Because of its reactivity, it soon loses its characteristic properties. Storage for three months accompanied by frequent shaking with glass beads renders it insoluble in concentrated hydrochloric acid. After six weeks' contact with 1% ammonia, it becomes insoluble in hot 3% hydrochloric acid, this reagent causing peptisation instead. The composition of the hydrate was determined by drying to constant weight in a vacuum desiccator over phosphoric oxide; the results indicate the constitution $Al_2O_3+3H_2O$. The substance is quite stable in dry air up to 80°, but at higher temperatures it loses water.

The new preparation can be used as a basic absorption medium for enzymes. Towards amylase (pancreatic) and invertase (autolysed yeast) it is nearly as efficient an absorbent as preparation *B* previously described. H. H.

Chemical Properties of Disperse Substances. Disperse Aluminium Oxide. II. V. Kohlschütter and Nelly Neuenschwander (*Z. Elektrochem.*, 1923, **29**, 246—256).—In continuation of previous work (A., 1919, ii, 156), the authors have investigated the chemical properties of disperse aluminium hydroxide prepared from ammonium alum, aluminium sulphate, and basic aluminium acetate, and more especially the dependence of these properties on the mode of preparation of the disperse phase. All varieties of hydroxide were chemically dissolved by strong hydrochloric acid solution, the process of solution being preceded by swelling of the hydroxide. Sols were formed and chemical action occurred when the hydroxide was treated with sufficiently dilute acid. The production of a colloid occurred likewise as an intermediate stage in the process of solution. Whereas aluminium hydroxide was dissolved by strong solutions of sodium hydroxide, a sol was not produced by the action of a dilute solution of the latter. In contradistinction to this result, sols resulted from the action of either acid or alkali on disperse aluminium oxide prepared from fumes of the oxide. Sols resulting from the action of hydrochloric acid were readily differentiated either visually or ultra-microscopically, their respective appearances depending on the mode of preparation of the dried gel. A colloid was not

produced by the action of dilute sulphuric acid on the disperse phase, although a certain amount of chemical action occurred.

J. S. G. T.

Aluminium Antimonides. G. G. URAZOV (*J. Russ. Phys. Chem. Soc.*, 1919, **51**, 461—471).—The system antimony–aluminium has been repeatedly studied and both Gautier (A., 1896, ii, 602) and Campbell and Matthews (A., 1902, ii, 399) conclude that a compound, AlSb, is formed, whilst the former author also suggests the existence of another compound corresponding with 69·27% by weight of aluminium or $Al_{10}Sb$, owing to a second break in the cooling curves at that point. The existence of the first, but not the second, compound is also confirmed by the microscopic examination of the alloy; this divergence between the results obtained by two different methods is explained by Tammann (A., 1906, ii, 88) by the supposition that the formation of the compound AlSb takes some time and this accounts for the existence of secondary breaks in the cooling curves.

In the present investigation, cooling curves for alloys of aluminium and antimony were constructed, the alloys being kept in the molten state for varying lengths of time. If the observations were made immediately after the contents of the crucible, consisting of equal weights of the components, became homogeneous, three breaks in the curves were observed, corresponding with the separation of AlSb (880°), pure aluminium (653°), and pure antimony (631°), respectively; the latter two phases are not miscible at temperatures near their respective melting points. Keeping the alloy in a molten condition at about 1100° for half an hour is sufficient to ensure the complete interaction of the components and the cooling curve no longer shows a break corresponding with the separation of antimony. The separation of the solid AlSb from an equimolecular mixture takes place at 976°.

A fusibility curve of mixtures of the compound AlSb with aluminium and antimony was constructed and is shown to be of simple character, the compound being unable to form solid solutions with either component; it is also practically insoluble in either component at temperatures near the melting point of the latter.

G. A. R. K.

Atomic Weight of Gallium. THEODORE W. RICHARDS and WILLIAM M. CRAIG (*J. Amer. Chem. Soc.*, 1923, **45**, 1155—1167).—The atomic weight of gallium has been determined by means of the analysis of gallium chloride. The starting material was 60 kg. of non-volatile residues obtained from the distillation of zinc which contained about 60 g. of gallium. The metal was dissolved in 500 g. portions in dilute nitric acid and treated with a slight excess of dilute sulphuric acid to precipitate most of the lead. The filtrate was evaporated until copious fumes of sulphur trioxide were evolved, cooled, and the semi-solid residual mass poured into water to make approximately a 5*N*-solution of sulphuric acid. After removal of the precipitated lead sulphate, the solution was treated with hydrogen sulphide, which removed the rest of the

lead and traces of copper and other heavy metals. The filtrate was diluted ten times, raised to the boiling point, and again treated with hydrogen sulphide, whereby most of the arsenic was removed. The filtrate was boiled and treated with sodium carbonate until a precipitate was barely perceptible. Gallium hydroxide was precipitated from the neutral solution by the addition of ammonium hydroxide, care being taken not to use an excess of ammonia. The gelatinous precipitate was washed by decantation and contained chiefly the hydroxides of gallium, indium, and zinc. The precipitate was treated with excess of potassium hydroxide, which dissolved the gallium and zinc and a little of the indium. The alkaline solution was neutralised with sulphuric acid and then treated with ammonia until a precipitate barely began to form, ammonium sulphate was added, and the solution electrolysed with a current of 10 amperes, the cathode being a stout platinum rod 10 cm. long, and the anode a platinum foil. Metallic zinc and indium were first deposited, but as the deposit contained some gallium it was therefore dissolved and re-electrolysed separately. As the electrolysis proceeded, yielding more gallium, the boiling solution deposited on the bottom of the vessel an insoluble basic gallium ammonium sulphate as a fine, granular powder, whilst at the same time arsine was evolved. The basic salt, which contained practically all the gallium, was dissolved in a slight excess of potassium hydroxide and the gallium deposited electrolytically. The gallium was then treated with warm concentrated nitric acid to remove the more soluble metals, washed, and treated with dilute sulphuric acid. The metal at this stage may possibly contain traces of zinc and other metals. The metal obtained solidified slightly below the true melting point, 29·75°. It was therefore fractionally crystallised eight times and it then melted exactly at 29·75°. The purest crystals were heated at 800—850° in a silica boat for twenty-four hours, and the product remaining in the boat then failed to give spectroscopic evidence of the presence of zinc, arsenic, indium, or lead. The pure gallium was converted into chloride by the method previously described (A., 1919, ii, 157, 158; 1921, ii, 264) and fractionated by distillation and sublimation in chlorine, in nitrogen, and in a vacuum. The salt was analysed by essentially the same method as that used in the analysis of aluminium bromide and as the mean of four determinations gave the value gallium=69·716, the extreme values being 69·707 and 69·722. The value was calculated on the assumption that chlorine=35·458 and silver=107·88. J. F. S.

Phenomena of Hydrolysis of Aqueous Solutions of Ferric Chloride. E. Puxeddu (*Gazzetta*, 1923, **53**, i, 210—215).—The results of the author's experiments indicate that the hydrolytic phenomena of aqueous solutions of ferric chloride are far more complex than is indicated by previous investigations. The extent to which the hydrolysis takes place increases with the dilution to a maximum and subsequently diminishes. This is indicated by maxima of turbidity, of the variation with time of the electrical

conductivity, and of the number of mobile particles observable by means of the ultramicroscope. The variation of the conductivity with the time follows at 0° a totally different course from that observed at 25° (cf. Goodwin, A., 1897, ii, 16), the lag period preceding the initiation of the hydrolysis being immensely greater at the lower temperature. T. H. P.

The Ternary System Ammonium Chloride–Ferric Chloride–Water. FREDERICK WILLIAM JEFFREY CLENDINNEN (T., 1923, 123, 1338—1344).

Cobaltous Triple Nitrites, and a Sensitive Reaction for Potassium. V. CUTTICA (*Gazzetta*, 1923, **53**, i, 185—189).—By addition to a neutral solution of a cobaltous salt of a more concentrated solution of a lead salt and then of a large excess of alkali nitrite solution (cf. this vol., ii, 76, 77), the following compounds have been obtained as dark green, microcrystalline precipitates: $Co(NO_2)_2,Pb(NO_2)_2,2KNO_2$; $Co(NO_2)_2,Pb(NO_2)_2,2RbNO_2$; $Co(NO_2)_2,Pb(NO_2)_2,2NH_4NO_2$, and $Co(NO_2)_2,Pb(NO_2)_2,2TlNO_2$. The formation of these compounds probably occurs in two stages, the second stage being represented by the equation $K_2Co(NO_2)_4+K_2Pb(NO_2)_4=2KNO_2+[Co(NO_2)_6]^{K_2}_{Pb}$. These triple nitrites are highly stable in the air and exhibit marked resistance to the action of cold, dilute mineral acids.

The formation of cobaltous lead potassium nitrite serves as a means of detecting 1 part of potassium in 10,000 parts of solution. [Cf. *J.S.C.I.*, 1923, July.] T. H. P.

Phosphotungstates with $3WO_3$. F. KEHRMANN and R. MELLET (*Helv. Chim. Acta*, 1923, **6**, 443—449).—The sodium, potassium, and ammonium salts corresponding with the formula $3MO,P_2O_5,6WO_3$,aq. have now been prepared in the pure state and the series is definitely established (cf. this vol., ii, 77). Three mols. of water are firmly held in the series of salts as water of constitution. The sodium salt is prepared by the slow crystallisation of an aqueous solution containing sodium tungstate (3 mols.) and disodium hydrogen phosphate (1 mol.) neutralised with acetic acid. After five recrystallisations from water, it is pure. The sodium phosphotungstate crystallises in aggregates of white, striated prisms having the composition $3Na_2O,P_2O_5,6WO_3,3H_2O+13H_2O$. The *potassium* salt could not be prepared directly from its constituents, but was obtained by precipitating a solution of the sodium salt with potassium chloride. It is far less soluble than the sodium salt and forms brilliant, prismatic needles containing $3H_2O+11H_2O$. The *ammonium* salt, prepared from the sodium salt and ammonium chloride, crystallises in brilliant, short, stout prisms containing $3H_2O+6H_2O$. The free acid could not be prepared. The analysis of these salts, which offered some difficulty, will be fully described in a future paper. E. H. R.

The Relation of Actinium to Uranium. A. S. RUSSELL (*Nature*, 1923, **111**, 703—704).—From a consideration of the periods of corresponding members of the three disintegration series,

the following scheme giving the element, period, atomic number, radiation, and atomic weight is put forward: Actino-uranium-I; $>5\times10^9$ years; 92; α; 240. Uranium-Y_1; 25·5 hours; 90; β; 236. Uranium-Y_2; probably very short; 91; β; 236. Actino-uranium-II; $>2\times10^6$ years; 92; α; 236. Parent of proto-actinium; >20 years; 90; β; 232. Proto-actinium; $<1\cdot2\times10^4$ years; 91; α; 232. Actinium; 20 years; 89; β; 228. Radio-actinium; 19·5 days; 90; α; 228. Thus, although agreeing with Piccard in assuming that the parent substance of the actinium series is an isotope of uranium of atomic weight 240, the author differs from that investigator in believing that the atomic weight of actinium is not 232 but 228, and that uranium-Y is not the immediate parent of proto-actinium. In view of the fact that there are ten examples of similar types of radioactive transformation in which the period of the first β-particle is greater than that of the second, it is argued that the parent of protoactinium has a longer period than actinium, and consequently cannot be uranium-Y. It is claimed that the data given do not contravene the Geiger-Nuttal relation; they reduce the three exceptions to Fajan's α-ray rule to one only; and the two exceptions to the β-ray rule do not exist.

The ratio of the amounts of actino-uranium and uranium-I in uranium is experimentally found to be 5 : 95. Hahn's conclusion that uranium-X_1 breaks up dually is confirmed, and the periods of uranium-Y, uranium-Z and uranium-X_2 have been accurately determined to be 25·5 hours, 6·69 hours, and 70·5 seconds, respectively. It is pointed out that the branching ratio, given by Hahn as 996·5 : 3·5, is approximately equal to the reciprocal of the periods of the two substances formed, namely, uranium-X_2 and uranium-Z. A. A. E.

Revision of the Atomic Weight of Titanium. Analysis of Titanium Tetrachloride. GREGORY PAUL BAXTER and GEORGE JOSEPH FERTIG (*J. Amer. Chem. Soc.*, 1923, **45**, 1228—1233).—An account of preliminary work on the analysis of titanium tetrachloride made for the purpose of atomic weight determination. Titanium tetrachloride was purified by fractional distillation, using the method employed by Baxter, Weatherill, and Scripture in the distillation of silicon tetrachloride and tetrabromide (this vol., ii, 412). The pure titanium tetrachloride was sealed in small bulbs which were broken under 3N-nitric acid, treated with nearly the equivalent amount of silver nitrate, the exact equivalent point being determined nephelometrically. Six experiments to determine the ratio $TiCl_4$: 4Ag gave a mean value of 0·43957, the extremes being 0·43940 and 0·43967, which leads to the mean value 47·85 for the atomic weight of titanium, the extreme values being 47·89 and 47·78.

J. F. S.

Investigations of the Chromates of Thorium and the Rare Earths. I. The System Thorium Oxide–Chromic Anhydride–Water at 25°. HUBERT THOMAS STANLEY BRITTON (T., 1923, **123**, 1429—1435).

Thorium Molybdate, $Th(MoO_4)_2$. F. ZAMBONINI (*Compt. rend.*, 1923, **176**, 1473—1475).—Whilst the thorium molybdate is crystographically clearly distinct from calcium, strontium, barium, lead, cerium, lanthanum, and neodymium molybdates, the differences between corresponding angles are not greater than those sometimes observed between typical isomorphs. Mixed crystals of thorium and cerous molybdates were obtained containing in one case 1% of the cerium salt, in the other 6% of the thorium compound. The fact that tervalent and quadrivalent elements form such isomorphous crystals is considered to indicate the possibility of element 72 being found in conjunction with rare earths, themselves tervalent, although the new element is quadrivalent. H. J. E.

The Isotopes of Germanium. F. W. ASTON (*Nature*, 1923, **111**, 771).—By the use of an anode containing a fluorine compound of germanium, three isotopes of mass 70, 72, and 74, respectively, with intensity ratio 2 : 4 : 5 have been detected, the values being in reasonably good agreement with the accepted atomic weight. A. A. E.

Action of Vanadyl Trichloride and of Nitrosyl Chloride on Metallic Oxides. V. CUTTICA, A. TARCHI, and P. ALINARI (*Gazzetta*, 1923, **53**, i, 189—194; cf. Bassett and Taylor, T., 1911, **99**, 1402).—Vanadyl trichloride acts on magnesium oxide at the ordinary temperature giving a brick red, pulverulent substance which contains 12·4% Mg, 20·4% V, and 25% Cl and yields the hexavanadate, $Mg_2V_6O_{17},19H_2O$, when treated with water. In a sealed tube at 150—160°, vanadyl trichloride and cupric oxide give *copper chlorovanadate*, $Cu(VO_3)_2,CuCl$, as a dark green powder. Similarly lead oxide yields the *chlorovanadate*, $Pb(VO_3)_2,PbCl_2$, as a brick-red powder. At the ordinary temperature, vanadyl trichloride and thallous oxide yields *thallous chlorovanadate*, $Tl_2O,VOCl_3$, as a deep chestnut-brown powder (cf. Ephraim, A., 1903, ii, 487); treatment of this compound with water gives vanadyl chloride and the polyvanadate, $Tl_2O,3V_2O_5$. From the instability of these compounds towards water, it is probable that the chlorine is combined with the vanadium, the structures being $Cu{<}^{O}_{O}{>}VOCl,CuVO_3$, $Pb{<}^{O}_{O}{>}VOCl$, and $VCl_3(OTl)_2$ (cf. Ephraim, *loc. cit.*).

The action of nitrosyl chloride on cupric oxide yields an unstable compound, which decomposes rapidly in the air, giving cupric chloride. With cuprous chloride or oxide, nitrosyl chloride gives the compound $Cu_2Cl_2,NOCl$ (cf. Sudborough, T., 1891, **59**, 655). Thallous oxide and nitrosyl chloride yield the red *compound*, $TlCl_3,3NOCl$, which is moderately stable in the air, but in a vacuum gradually decomposes, with formation of thalloso-thallic chloride. T. H. P.

Platinum Complexes. L. A. TSCHUGAEV (*J. Russ. Phys. Chem. Soc.*, 1920, **51**, 193—231).—[With M. S. GRIGORIEVA.] cis-*Platinodiamminedihydrazine chloride*, $\left[{}^{NH_3}_{NH_3}{>}Pt{<}^{N_2H_4}_{N_2H_4}\right]Cl_2$,

white crystals, is prepared by grinding up Peyronier's chloride, $\left[{NH_3 \atop NH_3}>Pt<{Cl \atop Cl}\right]$, with hydrazine hydrate. This compound decomposes in cold aqueous solution within fifteen to twenty minutes; when heated, decomposition is almost immediate, with the liberation of platinum black. The dry salt may be kept without decomposition for a few days. The *chloroplatinite*, green crystals, is prepared, and a *dihydrochloride*, $\left[{NH_3 \atop NH_3}>Pt<{NH_2 \cdot NH_3 \atop NH_2 \cdot NH_3}\right]Cl_4$, white crystals, is obtained by the addition of hydrochloric acid to a solution of the chloride. The dihydrochloride may be kept for some months without noticeable decomposition, and the original chloride is regenerated from it by the addition of the calculated quantity of sodium hydroxide. The addition of potassium chloroplatinite to the dihydrochloride gives a *compound*, $\left[(NH_3)_2Pt<{N_2H_4 \atop N_2H_5}\right]_2(PtCl_4)_3$, violet prisms. The chloride on warming with hydrochloric acid yields Peyronier's chloride in the following way: $[(NH_3)_2Pt(N_2H_4)_2]Cl_2 \longrightarrow [(NH_3)_2Pt(N_2H_5)_2]Cl_4 \longrightarrow [(NH_3)_2PtCl_2]+2N_2H_4,2HCl$. trans-*Platinodiamminedihydrazine chloride* is obtained in the same way as the *cis*-compound from Reise's chloride II, $\left[{NH_3 \atop Cl}>Pt<{Cl \atop NH_3}\right]$, and forms an *iodide* and a *chloroplatinite* similar in properties to those of the *cis*-compound. With hydrochloric acid a *dihydrochloride*, white needles, is obtained, and the further action of hydrochloric acid is to regenerate Reise's chloride II, in an analogous way to the *cis*-compound. *Platinotetrahydrazine chloride*, $[(N_2H_4)_2Pt(N_2H_4)_2]Cl_2$, white needles, decomposing within a few days of preparation, is prepared by the action of hydrazine hydrate on platinoditripropylammine tetrachloride, $[(C_3H_7)_3NH]_2PtCl_4$, and can also be obtained from the compounds of platinous chloride with thio- and dithioethers, $[Pt2R_2SCl_2]$ and $[PtRS(CH_2)_2SRCl_2]$. The *chloroplatinite*, deep red crystals, and the *iodide*, silky needles, of the above compound are prepared, and a *compound*, $Pt(N_2H_4)_2Cl_2,2HCl,2H_2O$, white crystals, is obtained by the action of hydrochloric acid. cis-*Platinodinitrodihydrazine*, $[(N_2H_4)_2Pt(NO_2)_2]$, white crystals, is obtained by warming potassium platinonitrite with hydrazine hydrate. This compound is changed by acids into a *substance*, $\left[{NH_2 \atop NH_2}>Pt<{NO_2 \atop NO_2}\right]$ in which both nitrogen atoms of a hydrazine molecule are united to the platinum.

[With I. I. Tschерniaev.]—*Platino*-cis-*diamminedihydroxylamine chloride*, $\left[{NH_3 \atop NH_3}>Pt<{NH_2 \cdot OH \atop NH_2 \cdot OH}\right]Cl_2$, white needles, is prepared by the action of aqueous hydroxylamine on Peyronier's chloride, $[(NH_3)_2PtCl_2]$, and is ionised in solution. Its *chloroplatinite*, purple needles, and *chloropalladite*, red needles, both soluble in hot water, and ionised in solution, are prepared. trans-*Platinodiamminedihydroxylamine chloride*, colourless prisms, is obtained in an analogous way to the *cis*-compound, from Reise's chloride, $\left[{NH_3 \atop Cl}>Pt<{\ \atop NH_3}\right]$,

and is less soluble than the *cis*-compound, the salt being fully ionised in solution. On warming with hydrochloric acid, it regenerates Reise's chloride. The *trans*-isomeride may also be obtained by the action of anhydrous liquid ammonia on *trans*-platinodihydroxylamine dichloride, $\frac{Cl}{OH\cdot NH_2}>Pt<\frac{NH_2\cdot OH}{Cl}$. Lossen (*Annalen*, 1871, **160**, 242) obtained a substance by this reaction, using aqueous ammonia, which he erroneously described as the *trans*-isomeride, and this is now shown to be $\left[\frac{OH}{OH\cdot NH_2}>Pt<\frac{NH_2\cdot OH}{Cl}\right]$, which on warming with hydrochloric acid regenerates the *trans*-platinodihydroxylamine dichloride, and is probably formed by the hydrolysis of the *trans*-isomeride. The *chloroplatinite*, green needles, and the *chloropalladite*, olive-green crystals both soluble in hot water, are prepared. trans-*Platinodichloroamminehydroxylamine*, $\frac{NH_3}{Cl}>Pt<\frac{Cl}{NH_2\cdot OH}$, yellow crystals, soluble in hot water, is prepared from *cis*-platinodiamminedihydroxylamine chloride by warming with hydrochloric acid; prolonged heating with the latter results in the production of Kossa's acid, $[Pt(NH_3)Cl_3]H$. *Platinotriamminehydroxylamine chloride*, $\left[(NH_3)_2Pt<\frac{NH_3}{NH_2\cdot OH}\right]Cl_2$, white plates, soluble in water, is obtained by heating the mixed chloride, $\frac{NH_3}{Cl}>Pt<\frac{Cl}{NH_2\cdot OH}$, with liquid ammonia in a sealed tube; on warming with hydrochloric acid it yields Cleve's chloride,

$$[Pt3NH_3Cl]Cl.$$

Its *chloroplatinite*, pale green needles, yields similarly Cleve's chloroplatinite, $[ClPt3NH_3]_2PtCl_4$. *Platinoamminetrihydroxylamine chloride*, white crystals, is prepared by heating the mixed chloride with hydroxylamine, and its *chloroplatinite*, and *chloropalladite*, purple crystals, are prepared. trans-*Platinodipyridinedihydroxylamine chloride*, $\left[\frac{Py}{OH\cdot NH_2}>Pt<\frac{NH_2\cdot OH}{Py}\right]Cl_2$, white crystals, is obtained by warming pyridine with *trans*-platinodihydroxylamine dichloride; on warming with hydrochloric acid, it yields *trans*-platinodipyridine dichloride. Its *chloroplatinite*, pink prisms, is prepared. *trans*-Platinodihydroxylamine dichloride is prepared by warming platinotetrahydroxylamine chloride with hydrochloric acid. This substance is little ionised in solution, and is capable of forming double salts with Reise's chloride I,

$$[Pt(2NH_2\cdot OH)Cl_4]Pt,4NH_3,2H_2O,$$

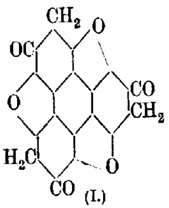
pale yellow crystals, and with cæsium chloride, $[Pt(2NH_2\cdot OH)Cl_4]Cs_2$, pale yellow crystals. R. T.

Mineralogical Chemistry.

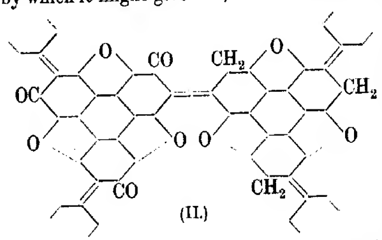
Structure of Native Platinum. S. F. SCHEMTSCHUSCHNY (*J. Russ. Phys. Chem. Soc.*, 1919, **51**, 417—460).—The physical properties, microstructure, and chemical composition of a number of samples of native platinum from the Urals were studied. It is concluded that platinum found in massive rocks is of magmatic origin (cf. Beck, *Ber. Ges. Wiss. Leipzig*, 1907, **59**, 387). Thus, it possesses a microstructure similar to that of alloys, the components of which form solid solutions of various concentrations; the hardness of the samples is greater than that of pure platinum, being a solid solution of metals of the platinum group and also iron, in platinum; the presence of occluded air bubbles and of crystals of the compound OsI_2 is also in accordance with that view.

G. A. R. K.

The Chemical Structure of Coal. WALTHER SCHRAUTH (*Brennstoff-Chem.*, 1923, **4**, 161—164).—The author has previously suggested (A., 1923, i, 443) that the fundamental unit of lignin is a keto-derivative of a hydro-9 : 10-benzophenanthrene in which the three outside benzene rings are linked up through oxygen (formula I). Such a molecule would possess great reactivity. It could, by enolisation, give rise to esters and ethers, the occurrence of which in lignin is established. Carboxylic acids of high molecular weight, similar in character to the humic acids, might also be derived from it, whilst reduction might lead to the replacement of the oxygen in the furan rings by hydrogen. It would be particularly susceptible to various condensation processes by which it might give rise, in the course of coal formation, to new molecules of unlimited size (type II), containing possibly also sulphur and nitrogen, which would finally, by elimination of carbon dioxide and water, lead to products not unlike coal itself. Not only does the hydrogenation of coal indicate the presence in it of unsaturated linkings, but the decomposition products formed under the conditions of temperature and pressure attendant on the formation of the coal itself and, in a more marked degree, by low temperature carbonisation, are directly derivable from a molecule of the above type. The occurrence of purely aromatic hydrocarbons, such as



(I.)



(II.)

naphthalene and anthracene, as primary products of low temperature carbonisation is not to be expected, and the fact that low temperature tars do not contain these but are mainly composed of alkylated phenols and hydrogenated hydrocarbons supports the author's argument. Further support is provided by the presence, in these tars, of unsaturated aliphatic hydrocarbons and of acetone. An exact examination of the higher constituents of low temperature tars is at present lacking, but the results so far obtained appear to be in agreement with the above formulation which may thus, at least, be taken as a working hypothesis. W. T. K. B.

Argentojarosite, a New Silver Mineral. WALDEMAR T. SCHALLER (*J. Washington Acad. Sci.*, 1923, **13**, 233). C. A. SCHEMPP (*Amer. J. Sci.*, 1923, [v], **6**, 73—75).—Small, yellow to brown, hexagonal, optically uniaxial and negative scales from Dividend, Utah, resemble jarosite in appearance, but have the composition $Ag_2O,3Fe_2O_3,4SO_3,6H_2O$, with Ag_2O 18, Fe_2O_3 43, SO_3 28, H_2O 10% and some K_2O and PbO. This is the first record of a silver mineral containing oxygen, and it is sufficiently abundant to be worked as an ore. L. J. S.

Analytical Chemistry.

Polarimetric Estimation of Acidic and Basic Groups in Various Types of Compound. I. Basic Groups. J. GROOT (*Biochem. Z.*, 1923, **137**, 517—530).—By working with sucrose solutions of a constant concentration, the relation between the velocity constant of inversion, K, and the normality N, of the hydrochloric acid is determined over a given range. The function is not quite a straight line, but can be represented by an equation of the type $K=aN+bN^2$, where a and b are constants. Having evaluated these constants, the velocity of inversion by hydrochloric acid is determined in the presence of a small proportion of a basic substance, as, for instance, *o*-aminobenzoic acid. The effective hydrochloric acid concentration is thus calculated and hence the proportion inactivated by the *o*-aminobenzoic acid is known.

H. K.

Use of Potassium Ferrocyanide in Analysis. C. PORLEZZA (*Ann. di Chim. Applic.*, 1923, **13**, 48—53).—The formation of a blue precipitate in an acid solution of potassium ferrocyanide (cf. Tarugi, Report VI. Internat. Congress Applied Chem., Rome, 1906) does not occur in the dark, but takes place fairly rapidly in diffused light in presence of air, hydrocyanic acid being liberated in small proportion. The resultant liquid yields a precipitate of ferric hydroxide when treated with excess of sodium hydroxide. Special precautions must therefore be taken in applying analytical processes involving the use of ferrocyanide in acid solutions (Fresenius and Hintz, A., 1895, ii, 536; Browning, A., 1921, ii, 279; Browning and Porter, A., 1921, ii, 265). The possible causes of the formation of the blue precipitate are discussed. T. H. P.

Use of Bromate in Volumetric Analysis. I. Stability of Bromic Acid in Boiling Solutions. G. FREDERICK SMITH (*J. Amer. Chem. Soc.*, 1923, **45**, 1115—1121).—With the object of ascertaining whether or no potassium bromate is a suitable volumetric reagent in reactions where it is necessary to add an excess of the reagent, the stability of solutions of potassium bromate ($0.025N$) which had been acidified on boiling has been investigated. It is shown that solutions of bromate acidified with perchloric acid, nitric acid, or acetic acid, so that the concentration of the acid is $2N$, are not decomposed on boiling or five minutes; sulphuric acid and phosphoric acid solutions are much less stable. The presence of free bromine has no effect except with acetic acid, but the presence of 10 mg. of potassium chloride causes a slight reduction. The amount of bromide in bromate may be estimated by acidifying the solution and distilling the bromine liberated. Barium bromate may be substituted for potassium bromate with equally good results.

J. F. S.

The Error in Bang's Micro-estimation of Chloride. II. RICHARD PRIGGE (*Biochem. Z.*, 1923, **137**, 484—488).—One extraction of blood with alcohol in the Bang micro-method is insufficient to remove the whole of the chloride. A second extraction in which the drop of blood is left in contact with the alcohol for three hours is adequate, but contact for fifteen seconds is insufficient.

H. K.

The Titration of Hypochlorous Acid. A. SCHLEICHER (*Z. anal. Chem.*, 1923, **62**, 329—335).—The low results obtained by Clarens (A., 1914, ii, 741) in using Penot's method of estimating hypochlorous acid by titration with sodium arsenite are shown not to be due to loss of chlorine dioxide. Good results can be obtained by mechanically stirring the solution during the addition of arsenite; no preliminary test is then necessary. Addition of potassium bromide as indicator invariably leads to low results. Electrometric titration, using a solution that has been carefully titrated in the usual way with iodide-starch paper as indicator, as a comparison electrode is very satisfactory.

A. R. P.

Free Sulphur in Motor Fuels, etc. W. R. ORMANDY and E. C. CRAVEN (*J. Inst. Petroleum Tech.*, 1923, **9**, 133—139).—To estimate free sulphur in light petroleum, etc., 100 c.c. of the sample are shaken thoroughly in a stoppered bottle for fifteen minutes with about 3 c.c. of mercury; 10 c.c. of dilute hydrochloric acid (1 : 100) are then added, the mixture is again shaken, and the mercury sulphide formed collected on a moistened asbestos filter. The filter and precipitate are washed with dilute hydrochloric acid, then transferred to a beaker, and the sulphide is oxidised and dissolved by heating with hydrochloric acid and a small quantity of potassium chlorate. The solution is filtered and the sulphuric acid in the filtrate is estimated by precipitation as barium sulphate. Various brands of "petrol" examined contained from a trace to 6·3 mg. of sulphur per 100 c.c.

W. P. S.

Estimation of Inorganic Impurities in Organic Compounds Soluble with Difficulty in Water, such as Sulphuric Acid in Picric Acid. T. S. Patterson and K. L. Moudgill (*J. Soc. Chem. Ind.*, 1923, **42**, 211—212T).—Fifty g. of picric acid are placed in a large boiling tube together with 100 c.c. of water, the tube is immersed in a bath of concentrated potassium carbonate solution heated at 130°, and a current of steam is passed into the mixture for thirty minutes. The supernatant liquid is then decanted and the residual picric acid treated twice in a similar way. The decanted liquids are filtered and the sulphuric acid is estimated in the usual manner by precipitation as barium sulphate. An alternative method consists in mixing 100 g. of picric acid with 200 c.c. of nitrobenzene, heating the mixture at 40°, and shaking it with 80 c.c. of water. The aqueous portion is then removed and the extraction repeated four times. The combined aqueous portions are filtered and the sulphuric acid is estimated in the filtrate. W. P. S.

Sensitivity of the Reaction between Silver Nitrate and a Sulphite. O. Hackl (*Chem. Zeit.*, 1923, **47**, 466).—Investigation of the reaction which occurs when a few drops of a solution of silver nitrate are added to a solution containing sodium sulphite shows that the appearance of a precipitate is dependent, not merely on the concentration of the solution of sodium sulphite, but also on its volume. For instance, addition of silver nitrate to 100 c.c. of a solution containing 0·00315 g. of $Na_2SO_3,7H_2O$ yielded no permanent precipitate, but a distinct precipitate was observed when 1 c.c. of a similar solution was used. By means of silver nitrate, it is possible to detect not less than 0·001 g. of SO_3 (as sulphite) in 10 c.c. of water or 0·0001 g. of SO_3 in 1 c.c. A. J. H.

New Colour Reaction for Detecting Nitrous Acid. As. Zlataroff (*Z. anal. Chem.*, 1923, **62**, 384—385).—Nitrites may be detected in waters by treating 10 c.c. with 1 to 2 c.c. of a 0·0025% aqueous solution of Neutral red followed by 2 to 3 c.c. of dilute sulphuric or hydrochloric acid. A deep blue colour shows the presence of nitrites. The method will detect 0·00005 g. of nitrous acid in 1 litre of water, and is not affected by the presence of iron, manganese, or other metallic salts that occur in natural waters. A. R. P.

Estimation of Phosphoric Acid in Milk and its Application to the Detection of Added Water. A. Kling and A. Lassieur (*Ann. Falsif.*, 1923, **16**, 141—146).—When a mixture of phosphoric acid solution, a mineral acid, sodium molybdate solution, and ether is shaken and allowed to separate, three layers are formed, an upper ethereal layer, an intermediate aqueous layer free from phosphoric acid, and a lower layer consisting of a yellow liquid (*d* 1·23); the volume of this yellow liquid is proportional to the amount of phosphoric acid present. To estimate phosphoric acid in milk, the ash of the latter is fused with a small quantity of sodium nitrate, the fused mass is dissolved in 2 c.c. of water and 2 c.c. of hydrochloric acid (1 : 3), the solution is

filtered and the filter washed first with 10 c.c. of dilute hydrochloric acid and then with 10 c.c. of water. The filtrate is transferred to a pear-shaped bulb provided at its lower end with a narrow graduated stem, 7 c.c. of ether are added (or a quantity more than sufficient to saturate the solution), 15 c.c. of sodium molybdate solution (100 g. of molybdic acid and 32 g. of sodium carbonate per litre) are introduced slowly whilst the mixture is shaken, and the tube and its contents are submitted to centrifugal action for two minutes. The volume of the yellow liquid is then noted. The value of each division of the graduations, in terms of phosphoric acid, is determined by using a standard phosphoric acid solution. It is suggested that the quantity of phosphoric acid in milk may be used as a basis in the detection of added water in a sample. W. P. S.

Volumetric Method for the Estimation of Phosphorous Acid in the Presence of Phosphoric Acid. A. WINGLER (*Z. anal. Chem.*, 1923, **62**, 335—337).—A measured quantity of the solution containing the mixed acids is treated with a small excess of a saturated solution of bromine in water and the mixture is left for ten minutes in a dark place. Excess of bromine is removed by passing a current of air through the solution until it becomes colourless. The liquid is titrated with $N/10$-sodium hydroxide solution first with methyl-orange then with phenolphthalein. The process may be represented by the equation: $H_3PO_3+H_2O+Br_2=H_3PO_4+2HBr$. The first end-point is obtained when all the hydrobromic and one-third of the total phosphoric acid present are neutralised, and the second end-point when another one-third of the phosphoric acid is neutralised. From these figures the amount of each acid originally present is then readily calculated. A. R. P.

New Method of Estimating Arsenic in Steels. C. MAZZETTI and P. AGOSTINI (*Gazzetta*, 1923, **53**, i, 257—261).—The steel is dissolved in aqua regia, the solution evaporated to dryness, and the residue dissolved in hydrochloric acid, the insoluble silica and carbon being removed by filtration. The filtrate is treated with a hydrochloric acid solution of stannous chloride, and the precipitated arsenic filtered off under slight suction and washed free from iron. The filter is shaken with water until the paper is pulped, the arsenic being then dissolved in standard iodine solution, and the liquid titrated with standard arsenite solution in presence of sodium phosphate or sodium hydrogen carbonate and starch paste until a yellowish-pink coloration is obtained (cf. Andrews and Farr, A., 1909, ii, 437). [Cf. *J.S.C.I.*, 1923, July.] T. H. P.

Estimation of Carbon in Vegetable Mould. L. J. SIMON (*Compt. rend.*, 1923, **176**, 1409—1411).—The author has now applied the method of sulpho-chromic oxidation (A., 1922, ii, 593) to the estimation of carbon in vegetable mould, and details are given of experiments on three types of soil, (*a*) from an ordinary garden, (*b*) of a putty-like nature, and (*c*) one rich in humus. The

values obtained by the use of chromic acid are low when compared with the standard copper oxide method, but on using silver dichromate as the oxidising agent more accurate results follow. It is suggested that the chromic acid "oxidation deficit" (this vol., i, 81) may afford an indication of the nature of certain substances present in the soil. The method is stated to be simple and rapid. H. J. E.

A Method for the Estimation of Dissolved Carbon Dioxide. F. G. HALL (*J. Biol. Chem.*, 1923, **55**, 751—755).—The method is specially designed for the estimation of carbon dioxide liberated by aquatic animals in respiration experiments. The gases are extracted from the solution by repeated evacuation; measurement of their volume before and after absorption of carbon dioxide gives the volume of the latter. The evacuation tube is constructed on the principle of Van Slyke's blood gas apparatus, but is of larger dimensions. E. S.

The Estimation of Silica in Waters. F. DIÉNERT and F. WANDENBULCKE (*Compt. rend.*, 1923, **176**, 1478—1480).—Small quantities of silica may be estimated colorimetrically by means of ammonium molybdate; heating the solution is obviated in the production of the colour by using this reagent in the presence of a mixture of sulphuric and nitric acids. The method permits of the differentiation of colloidal and non-colloidal silica, and shows that the latter form is that which normally occurs in waters. The method may be used for studying the change from the colloidal to the non-colloidal state. Experimental details are given. [Cf. *J.S.C.I.*, 1923, July.] H. J. E.

The Estimation of Potassium by means of Sodium Cobaltic Nitrite. EMM. POZZI-ESCOT (*Bull. Soc. chim. Belg.*, 1923, **32**, 227).—In reference to Clerfeyt's paper on this subject (this vol., ii, 181) the author directs attention to the fact that all the details of the method were published by de Koninck several years ago, and that this method for the estimation of potassium has been officially adopted in the United States for some time. G. F. M.

Volumetric Method for the Estimation of Potassium. M. BULLI and L. FERNANDES (*Ann. di Chim. Applic.*, 1923, **13**, 46—48).—Potassium may be estimated accurately by precipitating it as the triple nitrite, $[Co(NO_2)_6]PbK_2$, and titrating the nitrous residue in the precipitate with permanganate solution. [Cf. *J.S.C.I.*, 1923, July.] T. H. P.

Estimation of Calcium, Magnesium, Potassium, and Sodium in Human Blood. A. MIRKIN and S. J. DRUSKIN (*J. Lab. Clin. Med.*, 1923, **8**, 334—339).—Citrated blood is oxidised by heating with a mixture of fuming nitric acid and concentrated sulphuric acid. After evaporation, a little ammonium hydrogen carbonate is added, volatile ammonium sulphate being formed. In the residue, calcium and magnesium are precipitated by ammonium stearate solution and weighed as stearates. These are dissolved

in $0{\cdot}01N$-sulphuric acid, the precipitated stearic acid removed by filtration, and the excess of acid titrated with $0{\cdot}01N$-sodium hydroxide solution. Hence the respective amounts of calcium and magnesium can be calculated. The filtrate from the precipitated stearate is evaporated to dryness, ignited, and the alkali sulphates are weighed; an estimation of the sulphate present gives the proportions of sodium and potassium. CHEMICAL ABSTRACTS.

Volumetric Method for the Estimation of Magnesium. M. BULLI and L. FERNANDES (*Ann. di Chim. Applic.*, 1923, **13**, 44—45).—Magnesium may be estimated accurately by precipitation as magnesium ammonium ferrocyanide, and determination of the remaining excess of ferrocyanide in solution by titration with zinc sulphate. [Cf. *J.S.C.I.*, 1923, July.]

T. H. P.

Electrolysis of Zinc Oxide and Cadmium Oxide Fused in Sodium Hydroxide. R. SALANI (*Gazzetta*, 1923, **53**, i, 229—233; cf. this vol., ii, 54).—The author has investigated the conditions in which it is possible to separate zinc and cadmium electrolytically from a mixture of 5 g. of zinc oxide and 5 g. of cadmium oxide fused in 150 g. of sodium hydroxide. Graphite crucibles cannot be used as they suffer disintegration, and it is found most convenient to employ an iron crucible as anode and a strip of iron as cathode. T. H. P.

Detection of the Elements of the Hydrogen Sulphide Group with Especial Reference to Spot Tests. F. FEIGL and F. NEUBER (*Z. anal. Chem.*, 1923, **62**, 369—384).—One drop of a solution containing 2 mg. of mercury per 100 c.c. yields a distinct blue colour when placed on a filter-paper moistened with alcoholic diphenylcarbazide solution. Cadmium and copper interfere, but their sulphides are soluble in nitric acid. To distinguish mercurous from mercuric salts, the solution is shaken with a benzene solution of diphenylcarbazide. A blue benzene layer indicates mercuric salt, a flocculent precipitate at the interface between the liquids, mercurous salt. Lead, to the extent of 1 part in 33,000 parts, may be detected by the formation of a blue colour when a drop of the solution is placed on a filter-paper moistened with ammoniacal hydrogen peroxide, then, after some time, treated with a drop of an acetic acid solution of benzidine. Bismuth interferes, but lead may be detected in the presence of eleven times its weight of bismuth by carrying out the test with tetramethyldiaminodiphenylmethane instead of with benzidine. A spot test for bismuth consists in placing a drop of the solution on a paper moistened with a solution containing 1 g. of cinchonine (dissolved in very dilute nitric acid) and 2 g. of potassium iodide per 100 c.c. Bismuth gives an orange-yellow colour; if mercury, copper, and lead are present, the mercury forms a white spot inside the orange-yellow bismuth ring, lead gives a yellow ring outside this, and copper a brown ring outside the lead ring. Traces of copper may be detected by the blue colour produced by the addition of a drop of potassium

bromide solution, followed by a drop of benzidine hydrochloride solution to a drop of the test solution on filter-paper. Copper also gives a blue colour with potassium cyanide, and phosphomolybdic and hydrochloric acids which may be extracted from the solution by shaking with amyl alcohol. Cadmium gives a reddish-violet spot on a paper treated with a saturated solution of diphenylcarbazide in 90% alcohol that has been saturated with potassium thiocyanate and contains a little potassium iodide. Copper does not interfere; lead gives a yellow spot inside the cadmium coloration. Addition of stannous chloride to ammonium molybdate solution produces a blue colour which disappears on warming; if only 1 part of arsenic per million is present, the blue colour persists on warming. Antimonious and stannous chlorides both give a blue colour with a solution of phosphomolybdic acid, but only stannous chloride gives a similar reaction on a test-paper impregnated with ammonium phosphomolybdate. A. R. P.

Estimation of Tin in Wolfram. A Modification of Powell's Method. OCTAVIUS FRANCIS LUBATTI (T., 1923, **123**, 1409—1411).

Separation of Tin and Arsenic. LEROY W. MCCAY (*J. Amer. Chem. Soc.*, 1923, **45**, 1187—1191).—Quadrivalent tin and tervalent arsenic in dilute sulphuric or hydrochloric acid may be completely separated by treatment with hydrogen sulphide after the addition of a little hydrofluoric acid. The separation is effected by treating the solution in a platinum dish with 2—5 c.c. of 48% hydrofluoric acid, heating for a few minutes, and when cold diluting to 300 c.c. The solution is then treated with a rapid stream of hydrogen sulphide for thirty minutes, when arsenious sulphide alone is precipitated. The separation is both rapid and quantitative. J. F. S.

The Estimation of Ethylene and its Homologues in Primary Gas. H. TROPSCH and A. V. PHILIPPOVICH (*Brennstoff-Chem.*, 1923, **4**, 147—149).—Synthetic mixtures of ethylene and propylene were treated with sulphuric acid of concentrations from 80% to 99% in a 100 c.c. gas-absorption pipette filled with glass spheres of 1 cm. diameter. The quantities absorbed were noted after 0·5 minute, three minutes, five minutes, ten minutes. It was found that 87% sulphuric acid was very suitable for the separation of these gases, since in ten minutes it absorbed all the propylene and scarcely any of the ethylene. It is necessary that the ethylene should not greatly predominate in the mixture. Stronger acid absorbs too much ethylene, weaker acid absorbs propylene too slowly. The lighter homologues of ethylene behave like propylene, synthetic mixtures of air, argon, benzene, and ethylene treated with 87% sulphuric acid for fifteen minutes gave the correct absorption for ethylene when then shaken with bromine water. If the gas contain small amounts of benzene vapour the estimation of ethylene is not affected, as the benzene is absorbed by the 87% sulphuric acid, but if considerable amounts are present the method

fails, as the 87% acid only slowly absorbs benzene and some is left to be absorbed by the bromine water. These considerations, however, do not apply to primary gas, with which satisfactory results are obtained, as it contains but little benzene. T. S. W.

The Determination of *p*-Aminophenol in the Presence of Metol [*p*-Methylaminophenol Sulphate]. W. F. A. ERMEN (*Chemistry and Industry*, 1923, **42**, 538).—About 2 g. of the sample are dissolved in 100 c.c. of water with excess of hydrochloric acid, and titrated with $N/10$-sodium nitrite. The *p*-aminophenol is thus diazotised, whilst the metol forms a nitrosoamine which separates as white, crystalline hairs. Sodium acetate is then added, followed by a known excess of *m*-phenylenediamine, which couples with the diazo-compound; coupling is accelerated by warming to 25°. The mixture is cooled and excess of *m*-phenylenediamine titrated with freshly prepared N-diazobenzene solution. From the data thus obtained the amounts of *p*-aminophenol and metol present can be calculated. If the sample contains *s*-dimethyl-*p*-phenylenediamine, this must first be removed by washing with alcohol, in which its sulphate is readily soluble. The results obtained are accurate to within 1%. E. H. R.

Folin's Method for the Estimation of Uric Acid in Blood. A. SACHNOVSKA and IVAN ADAMOWITSCH ZALESKI (*J. Russ. Physiol.*, 1919, **2**, 36).—Slight modifications have been made in Folin's precipitation method (cf. this vol., ii, 196). The precipitated salts of uric acid are decomposed with hydrochloric acid instead of with hydrogen sulphide, and the final coloured solution is compared with a previously standardised blue glass. E. S.

The Estimation of Uric Acid in Blood. H. BROWN and G. W. RAIZISS (*J. Lab. Clin. Med.*, 1922, **8**, 129—134).—Adsorption of uric acid does not take place in the precipitation of blood proteins by the method of Folin and Wu. Equally good recoveries of added uric acid can be obtained either by Folin and Wu's or Benedict's methods. Folin and Wu's method gives correct results for blood uric acid, whilst the high results found with Benedict's method are due to interfering substances. Benedict's reagent is selective and yields results approximately similar to those of Folin and Wu only with high uric acid content. Benedict's method, owing to its speed and requirement of small quantities of blood, can be used for routine clinical analyses, but is not to be recommended for research purposes. CHEMICAL ABSTRACTS.

Exposure to Light as a Source of Error in Estimating Uric Acid by the Folin and Wu Method. HOBART ROGERS (*J. Biol. Chem.*, 1923, **55**, 325—331).—In the precipitation method of Folin and Wu (A., 1919, ii, 308; this vol., ii, 196), loss of uric acid results from exposure of the silver precipitate to light. Precautions should therefore be taken to avoid such exposure. E. S.

The Refractometric Estimation of Serum Proteins. BENJAMIN S. NEUHAUSEN and DAVID M. RIOCH (*J. Biol. Chem.*, 1923, **55**, 353—356).—In Reiss's method (A., 1904, ii, 303; *Z. Elektrochem.*, 1908, **14**, 613), more accurate results are obtained by deducting from the refractive index of the serum that for water plus 0·0022 for non-protein constituents and then dividing the remainder by 0·00194. Great accuracy cannot, however, be attained, since the last factor depends on the ratio globulin : albumin, which has been found to vary from 12 to 34%, although usually it is about 30%. E. S.

Modification of Brandberg's Method for the Estimation of Albumin in Urine. V. A. BOLOTOV (*J. Russ. Physiol.*, 1919, 2, 37).—Sulphosalicylic acid is used in place of nitric acid. E. S.

Test for Albumin and Other Urinary Proteins. WM. G. EXTON (*J. Amer. Med. Assoc.*, 1923, **80**, 529—530).—The urine is warmed with an equal volume of a reagent prepared as follows: 200 g. of sodium sulphate decahydrate are dissolved in 700—800 c.c. of water, cooled to 35°, 50 g. of sulphosalicylic acid are added with stirring until dissolution is complete, and the mixture is diluted to 1 litre. The turbidity developed in the presence of albumin is proportional to the concentration of the latter.
CHEMICAL ABSTRACTS.

Ostromisslenski's Reaction for Albumins. M. A. RAKUZIN (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 164—169).—The Ostromisslenski reaction for albumins is found to be given by proteins, and their salts, except the ammonium salt, by amino-acids, by amines and imines, but not by anilides or by "saccharin," by hydroxylamine and oxamide, but not by carbamide, and by alkaloids, with the exception of strychnine. It appears from this that, in general, the reagent (picramic acid) reacts with amino- and imino-groups. Pepsin and trypsin, which do not give the reaction in question, are therefore probably not albumins. R. T.

The Estimation by Van Slyke's Method of Free Amino-groups in Plant Globulins. A. I. OPARIN (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 266—271).—Van Slyke's method for the estimation of free amino-groups (A., 1911, ii, 779) is applied to the analysis of globulins extracted from various seeds, the time of reaction allowed being, not thirty minutes, as Van Slyke advises, but one hour, in view of the low reaction temperature necessary in this case. The total nitrogen content, determined by Kjeldahl's method, varied from 17·66 to 19·76% in the globulins examined, whilst the free amino-group nitrogen content varied from 0·349 to 0·504%. [Cf. *J.S.C.I.*, 1923, July.] R. T.

A Modification of Fuld's Method for the Estimation of Pepsin. RICH. EGE (*Z. physiol. Chem.*, 1923, **127**, 125—136).—Pepsin may be estimated by determining the amount of edestin

hydrolysed by it in a given time under standard conditions. Sodium chloride and sodium sulphate are added to the hydrolysed edestin until a precipitation occurs. The amount of salt required varies with the activity of the pepsin. W. O. K.

Starch for Use in Diastatic Assays. A. ASTRUC and A. RENAUD (*J. Pharm. Chim.*, 1923, [vii], **27**, 333—337).—Potato starch of commercially different kinds often gives widely varying results with the same pancreatin under the same conditions, and it may therefore appear good or bad according to the starch which happened to be used for the assay. The causes of this variation were investigated and neither the age of the potato from which the starch was derived nor the temperature used in drying was found to have any influence on the subsequent action of the enzyme. On the other hand, the method of preparation, particularly the character of the water used in washing and the sifting of the granules were sources of considerable variation. Preferably distilled water should be used in washing, or failing that spring water of constant composition, only granules passing a No. 100 sieve should be used in the assay, and their water content should be 7—8%. The method of preparing the mucilage is of minor importance, but a few minutes' heating are actually quite sufficient, and the formation of clots should, of course, be guarded against. G. F. M.

Estimation of Blood Catalase. Factors Affecting the Ratio between Quantity and Activity of this Enzyme. RUTH OKEY (*Amer. J. Physiol.*, 1922, **62**, 417—437).—Catalase activity is determined by titration of the undecomposed hydrogen peroxide with permanganate. Comparatively small variations in temperature may account for certain variations in catalase content previously reported by various investigators.

CHEMICAL ABSTRACTS.

Estimation of Neosalvarsan and its Absorption by Bacteria and Body-cells. E. REMY (*Biochem. Z.*, 1923, **137**, 133—143).—The colour produced by the coupling of diazotised neosalvarsan with alkaline resorcinol can be used for the colorimetric estimation of neosalvarsan. In urine, it can be estimated with an error of 3% at a dilution of 1 : 25,000 and in serum at 1 : 50,000. The azo-compound has been obtained crystalline, and can be identified in solution with other pigments by the spectroscope, absorption beginning at λ 560 $\mu\mu$. The fixation of neosalvarsan by bacteria or cells is an adsorption, but the adsorption isotherm only holds over small ranges. More adsorption takes place from water than from serum. H. K.

Refractometric Method for the Determination of Watering of Milk. MARIA CASTELLANI (*Ann. di Chim. Applic.*, 1923, **13**, 41—44).—A method is described for obtaining rapidly from milk a clear whey, refractometric examination of which serves to indicate if the original milk were watered. [Cf. *J.S.C.I.*, 1923, July.]

T. H. P.

General and Physical Chemistry.

Refraction and Absorption of Light by Zinc Blende at Temperatures up to 700°. Maria Mell (*Z. Physik*, 1923, **16**, 244—265).—Measurements were made of the refractive index and absorption of a specimen of zinc blende coloured slightly greenish-yellow, for temperatures ranging from $-80°$ to $700°$, and for wave-lengths between about 400 and 800 $\mu\mu$. The results indicate that in the visible spectrum the dispersion is normal and attributable principally to an oscillator with a frequency in the ultra-violet. The refractive index increases with temperature, and considerably more rapidly for light of short wave-length than for light of long wave-length. Thus for $\lambda=436\ \mu\mu$, the results show that the refractive index, n_t at $t°$, is given by $n_t=2\cdot4885\ (1+3\cdot8695\times10^{-5}t+17\cdot9\times10^{-9}t^2)$. Similarly, for $\lambda=546\ \mu\mu$, $n_t=2\cdot3870\ (1+2\cdot7508\times10^{-5}t+11\cdot1\times10^{-9}t^2)$, and for $\lambda=578\ \mu\mu$, $n_t=2\cdot3717\ (1+2\cdot5826\times10^{-5}t+9\cdot5\times10^{-9}t^2)$. The transparency of zinc blende increases with increasing wave-length of the light transmitted and decreases rapidly as the temperature increases. A minimum transparency observed in the mean or extreme red region of the spectrum is attributable to an impurity present in the blende. With increasing temperature, the region of selective absorption is displaced from the ultra-violet towards the visible region of the spectrum. J. S. G. T.

II. Spectrochemistry of Olefine-monocarboxylic Acids and their Derivatives. K. von Auwers (*Annalen*, 1923, **432**, 84—99).—The optical constants of a number of unsaturated monocarboxylic acids, esters, acid chlorides, and nitriles are tabulated and discussed.

For Δ^{α}-unsaturated acids, C:C·C(OH):O, the mean values for specific exaltation of molecular refraction and molecular dispersion are +0·9 and +33%, respectively, these figures being very similar to those, +0·9 and +30—40%, for the few Δ^{α}-unsaturated ketones, C:C·C(R):O, which have been investigated. Acids which contain the grouping C:C(R)·C(OH):O show a considerably smaller exaltation of molecular refraction, +0·6, but approximately the same exaltation of molecular dispersion. In general, therefore, not only may Δ^{α}-unsaturated acids be distinguished from isomerides in which there is no conjugation, but the presence of an α-substituent may likewise be detected. There are, however, exceptions; thus nonenoic acid, $CH_3\cdot[CH_2]_5\cdot CH{:}CH\cdot CO_2H$, and octadecenoic acid,

$$CH_3\cdot[CH_2]_{14}\cdot CH{:}CH\cdot CO_2H,$$

have abnormally low molecular refractions and molecular dispersions, and this is not due to the high molecular weight, since geranic acid, $CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CMe{:}CH\cdot CO_2H$, has large exaltations. It is also indicated that, in unsaturated acids, the grouping $CMe_2{:}C$, whether conjugated or not, causes a small increase in molecular refraction, and a large increase in molecular dispersion, in contrast

to the behaviour of this grouping in other compounds, *e.g.*, styrenes (but cf. Meyer, A., 1921, i, 855). The esters, acid chlorides, and nitriles have very similar optical properties.

A comparison between stereoisomeric Δ^{α}-unsaturated acids and esters reveals that the more stable of a pair of isomerides possesses a higher molecular refraction and molecular dispersion, although the difference is sometimes comparatively small. In accordance with this rule, of the β-chloro-derivatives of the two crotonic acids, the *iso*-derivative is the more stable. Stereoisomeric unsaturated acids, in which there is no conjugation, do not differ appreciably in either molecular refraction or molecular dispersion.

The following new data are recorded. Δ^1-Tetrahydrobenzoic acid has $d_4^{47\cdot2}$ 1·0717, hence $d_4^{47\cdot0}$ 1·0719, n_α 1·48576, n_{He} 1·49023, n_β 1·49882, n_γ 1·50705 at 47·0°, and its ethyl ester has b. p. 84—86°/12 mm., $d_4^{14\cdot15}$ 1·0032, d_4^{20} 0·998, n_α 1·46793, n_{He} 1·47167, n_β 1·47885, n_γ 1·48558 at 14·15°, n_{He}^{20} 1·4690. 1-Methyl-Δ^4-*cyclo*hexene-4-carboxylic acid has $d_4^{73\cdot7}$ 1·0085, hence $d_4^{69\cdot0}$ 1·0127, n_α 1·47283, n_{He} 1·47630, n_β 1·48496 at 69·0°. Its ethyl ester, prepared from the acid by means of absolute alcohol and concentrated sulphuric acid, had b. p. 115°/19 mm. (cf. Perkin and Tattersall, T., 1905, **87**, 1904), $d_4^{18\cdot0}$ 0·9762, hence $d_4^{18\cdot45}$ 0·9758, d_4^{20} 0·975, n_α 1·46413, n_{He} 1·46748, n_β 1·47473, n_γ 1·48126 at 18·45°, n_{He}^{20} 1·4695. A second sample, prepared from ethyl iodide and the silver salt, had $d_4^{17\cdot2}$ 0·9780, d_4^{20} 0·976, n_α 1·46551, n_{He} 46886, n_β 1·47622, n_γ 1·48263 at 17·2°, n_{He}^{20} 1·4676. The specific exaltation of molecular refraction for these compounds, +0·45, is decidedly smaller than for their acyclic homologues; the exaltation of molecular dispersion is likewise somewhat lower. W. S. N.

Double Refraction of Flowing Dyestuff Solutions. H. Freundlich, C. Schuster, and H. Zocher (*Z. physikal. Chem.*, 1923, **104**, 119—144; cf. A., 1916, ii, 65, 442).—Sols of benzopurpurin prepared in the cold show marked double refraction down to a concentration of 0·02% when given a rotatory motion; on warming, the solutions pass into the isotropic condition with the loss of the double refraction, but on cooling, the solutions revert to the anisotropic condition, more rapidly the greater the concentration; thus a 3·7% solution reverts in twelve hours, a 1·9% solution in two days, a 0·95% solution in four days, but solutions more dilute than 0·35% do not revert to the anisotropic condition even after many weeks. The addition of electrolytes to such dilute solutions brings back the double refraction. This process has been studied with various electrolytes, and it is shown that the nature of the anion has but little influence, whilst that of the kation is determinative, and, as in coagulation, the valency of the kation is mainly concerned. Inorganic univalent kations ($Li^{\cdot}$, $Na^{\cdot}$, $K^{\cdot}$, $Rb^{\cdot}$, and $NH_4^{\cdot}$), when added to a 0·25% sol, exhibit an optimum action at 40 millimols. per litre; bivalent kations ($Mg^{\cdot\cdot}$, $Ca^{\cdot\cdot}$, $Sr^{\cdot\cdot}$, $Ba^{\cdot\cdot}$, and $Cd^{\cdot\cdot}$) have their optimum action at 0·2 millimol. per litre. These concentrations are considerably lower than those at which turbidity is produced in the sols, the values being 110 and 1·0, respectively. With univalent and tervalent organic kations, the two points lie

so close together that the value for the double refraction cannot be definitely determined and the solutions are bleached by these kations. In the case of univalent inorganic kations, a region is found between 60 and 80 millimols. per litre where the activity of the electrolyte is much reduced, whilst with bivalent inorganic kations a similar region lies between 0·3 and 0·7 millimol. per litre. The Tyndall cone of the sols exhibits no such region, it increases in intensity regularly with increasing concentration of electrolyte. Colloids such as gelatin and albumin in certain concentrations prevent the appearance of the double refraction; they behave as protecting colloids. With respect to the production of turbidity, gelatin at first has a sensitising action and then a protective action. Doubly refracting sols containing electrolytes lose their refraction on warming, and a definite transition temperature exists in each case. Below this temperature, the solution may be heated for hours and still keep its double refraction, but above this temperature the double refraction vanishes. The transition temperature depends on the nature and concentration of the electrolyte, the age of the sol, and its previous treatment. The transition temperature is low for $Li^{\cdot}$ and $Na^{\cdot}$, higher for $K^{\cdot}$ and $NH_4^{\cdot}$, and considerably higher for $Ba^{\cdot\cdot}$ and $Mg^{\cdot\cdot}$, and it increases strongly with increasing concentration of the electrolyte and with increasing age. The transition temperature is reduced by shaking the solution with glass beads. The behaviour of the transition temperature can be regarded as due to a peptisation. The foregoing observations show that in all probability the appearance of the double refraction is due to the formation of long particles which are produced by an ordered coagulation, which is distinct from the usual unordered coagulation. The optimum of the double refraction is to be explained by the unoriented coagulation overcoming the oriented coagulation at higher concentrations of electrolytes. Concentrated benzopurpurin sols exhibit long particles in the ultramicroscope, and also a strong sparkling. No difference could be observed ultramicroscopically between the double refracting and non-refracting dilute solutions. The difference probably lies in the amicroscopic particles in these cases. Similar results have been observed with cotton-yellow *GX*, but here the process takes place more rapidly, so that the details, as in the case of benzopurpurin, are not readily observed.

J. F. S.

Colloidal Supports for [use in] obtaining Emission Spectra of Solutions. JACQUES ERRERA [with R. MASSAIN] (*Compt. rend.*, 1923, **176**, 1874—1876).—The electrolyte to be examined is allowed to penetrate into two cylindrical pieces of gelose, which are fitted into brass tubes and made the electrodes (cf. Gramont, A., 1908, ii, 3).

E. E. T.

Infra-red Spectra. Ultra-red Spectra of Various Substances and Ultra-red Absorption Spectra of Benzene and some of its Compounds. J. E. PURVIS (*Proc. Camb. Phil. Soc.*, 1923, **21**, 556—565).—The ultra-red emission spectra of a Nernst filament, a Nernst heater, a Welsbach light, a fish-tail burner, a Bunsen burner,

an acetylene jet and a carbon monoxide jet have been measured. The ultra-red spectra are plotted over the range 1—12μ. Curves showing the percentage of the ultra-red radiation of various wave-lengths, transmitted by iodobenzene, bromobenzene, and benzene, have been constructed from absorption data obtained with the liquids and vapours, and these results have been compared with those of Coblentz ("Infra-red spectra," Carnegie Inst. of Washington, 1905). J. F. S.

"Raies Ultimes" and Series Spectra. A. DE GRAMONT (*Compt. rend.*, 1922, **175**, 1025—1029).—The raies ultimes are those lines in the spectrum of an element which are the last to disappear as the content of the element in the substance examined approaches zero. These lines, both in the arc and spark spectra, always belong to the principal series of doublets, types [*H*] and [*K*] of calcium, and in the flame they belong to the type [*g'*] of calcium. They are always the first terms of the principal series, as is illustrated by a table of these lines. It should be possible to utilise the "raies ultimes" for the elucidation of the spectra of the elements for which the principal series spectra are not yet known, particularly those of iron, vanadium, titanium, etc. Mercury forms the sole exception to these rules, for the most sensitive line, λ 2536·5, does not belong to a principal series. W. E. G.

The Fundamental Orbit of Atoms. M. A. CATALÁN (*Anal. Fis. Quim.*, 1923, **21**, 162—165).—In the consideration of the spectrum of an element uncertainty may exist as to which term should be taken as the fundamental orbit of the atom. From a consideration of the values for the terms in a number of spectral series the following rules are deduced. 1. A member of a series must be considered as belonging to a principal or sharp series according to whether $+\nu=mp_i-ns$ or $+\nu=ns-mp_i$. 2. For equal values of m and n the terms ms are always less than the terms np_i, *i.e.*, $2s<2p_i$, $3s<3p_i$, and so on. 3. The first value of the sharp term corresponds with $m=1$, that of the principal term to $m=2$. A term $1S$ and a term $1s$ never occur together in the same spectrum. The single value for the sharp term for which $m=1$ is the fundamental orbit whether $1S$ or $1s$. The terms $1s$ in the case of the alkali metals and $1S$ in the case of the alkaline-earth metals permit the calculation of ionisation potentials in agreement with observation. G. W. R.

The Spectrum of Ammonia. W. B. RIMMER (*Proc. Roy. Soc.*, 1923, [*A*], **103**, 696—705).—Of the three bands associated with the spectrum of ammonia, the ultra-violet band with its centre at about λ 3360 has been investigated by Fowler and Gregory (A., 1918, ii, 282; 1919, ii, 253), and was found to be represented in the solar spectrum. Employing a concave grating giving a normal dispersion of about 5·5 Å. per mm. in the first order spectrum, the author has investigated the structure of the "Schuster bands" at $\lambda\lambda$ 5635 and 5670 Å., and of the α-band of Eder and Valenta in the spectrum of ammonia, the former bands being observed when a discharge is

passed through a vacuum tube through which a stream of ammonia flows, and the latter appearing in the spectrum of the flame of ammonia burning in oxygen. The Schuster bands showed no sign of resolution into lines, and it is probable that these bands do not occur in the solar spectrum. The α-band consists of about 3,000 lines. The wave-lengths and intensities of the strongest and sharpest of these are tabulated. No conclusive evidence that this band occurs in either solar or sunspot spectra was obtained. The observations, whilst confirming the suggestion of Lewis that the Schuster bands probably represent the true spectrum of ammonia and do not depend on dissociation for their emission, indicate further that the α-band is due to an emission centre representing a first stage of dissociation of the normal ammonia molecule into more stable forms, and the ultra-violet band is due to an emission centre which represents a still more advanced stage of dissociation, preceding complete dissociation into the constituent atoms.

J. S. G. T.

Influence of an Electric Field on the Series Spectrum of Helium. W. TSCHULANOWSKY (*Z. Physik*, 1923, **16**, 300—313).—The characteristics and behaviour of various series of single lines and doublets in the series spectrum of helium, and more especially the behaviour of the Bergmann series of single lines, $2P-m\Delta$, ($m=4$, 5, 6, 7) and the super-Bergmann series of doublets $2p_n-m\Delta_n$, ($n=1, 2$; $m=4$, 5), in an electric field, are discussed theoretically and practically. The author concludes that in the case of these lines, as in the cases of the series $2S-mD$, and $2P-mD$, additional lines, necessitating a third quantisation, appear when the helium source of radiation is excited in an electric field (cf. Takamine and Kokubu, A., 1919, ii, 125, 379). J. S. G. T.

The Ionisation of Helium and the Excitation of the Spectra of this Gas by Slow-moving Electrons. G. DÉJARDIN (*J. Phys. Radium*, 1923, **4**, 121—128).—The results obtained are in agreement with the experiments of Davies (this vol., ii, 281). The ionisation of helium under a pressure of a few tenths of a millimetre took place at 25·2 volts, and was accompanied by the simultaneous appearance of the orthohelium and parhelium spectra. When the pressure attained several mm. of mercury, an appreciable ionisation was produced at 20·4 volts, and again the appearance of the two series was noted. It was found impossible to excite these two series separately. When the pressure of mercury in the helium was allowed to rise to 0·1 μ, the ionisation commenced below 20·4 volts, but augmented rapidly when the potential passed this value. The band spectrum of helium is observed only when the pressure of the gas passes 3 mm. and the voltage exceeds 20·4 volts. The intensity increases with pressure. The results support the hypothesis of Lenz and Sommerfeld that the band spectra are due to a molecule He_2 resulting from the combination of two abnormal helium atoms. The spark spectrum are best visible at a pressure below 3 mm. and above 80 volts. At higher pressures this spectrum is masked by the band spectra. The rays of the Pickering series were not observed. W. E. G.

The Discontinuity K of Absorption of Krypton and Xenon. M. DE BROGLIE and A. LEPAPE (*Compt. rend.*, 1923, **176**, 1611—1612). —The position of discontinuity of absorption K in the X-ray spectrum does not appear to have been measured in the case of the rare gases. The authors found for krypton $\lambda = 0{\cdot}8648$ Å. $N=36$ and for xenon $\lambda=0{\cdot}3588$ Å. $N=54$. The measurements were made at atmospheric pressure in glass tubes of 20 cm. in length, the rays traversing the length of the tube. H. J. E.

Fine Structure of the Limits of High Frequency Absorption. L Limits of Xenon. A. LEPAPE and A. DAUVILLIER (*Compt. rend.*, 1923, **177**, 34—37).—The authors have measured, using a tungsten anti-cathode, the three L-limits of xenon and obtained the values: L_3 2272·4, L_2 2425·3 and L_1 2587·5 X units. E. E. T.

Quantitative Researches on the Ultra-violet Spark Spectra of Copper in Aluminium. XAVIER WACHÉ (*Compt. rend.*, 1923, **177**, 39—41).—In an alloy containing one metal in small quantities, the quantitative indications afforded by spectrum analysis on its composition depend on the nature (particularly the specific volume) of the metal present in the larger quantity. For equal concentrations, copper is less sensitive in aluminium than in a more dense metal such as zinc. A series of measurements of the spark spectra of various alloys of copper with aluminium was made, and it was found that the total copper spectrum is only obtained when copper is present to the extent of 60% of the total alloy. The spectrum of aluminium is also complete in these circumstances, being so with alloys possessing an aluminium percentage of as low as 20%. The copper spectrum is practically absent with copper present to the extent of only 5 parts in 10,000. E. E. T.

Wave-length Measurements in the Arc Spectra of Gadolinium and Dysprosium. C. C. KIESS (*U.S. Bur. Standards Sci. Paper*, 466, 1923, 695—706).—A list of 950 lines in the arc spectrum of gadolinium and of 800 in that of dysprosium is given from a wave-length of 550 Å. in the green and extending well into the ultra-red region. Most of the lines are faint, and a number have the appearance of band heads indicating that each element emits a faintly banded spectrum. The results obtained are in good agreement with those previously obtained by Eder (cf. A., 1918, ii, 189; 1919, ii, 381). A. R. P.

The Zeeman Effect in the Arc and Spark Spectra of Manganese. E. BACK (*Z. Physik*, 1923, **15**, 206—243).—A detailed account is given of an experimental investigation of the magnitude and other characteristics of the Zeeman effect exhibited by the various triplet and multiplet systems of lines in the arc and spark spectra of manganese determined by Catalán (A., 1922, ii, 726). Interpreted by means of Landé's theory (*Z. Physik*, 1923, **15**, 189), certain series differences determined by Catalán are considered, contrary to the conclusion of the latter, to afford evidence of a fundamental difference in the spectra of Mn and Mn^+. J. S. G. T.

Regularities in the Arc Spectrum of Iron. F. M. WALTERS (*J. Washington Acad. Sci.*, 1923, **13**, 243—252).—Two hundred and twelve lines of the spectrum of iron have been classified into multiplets. The correlation of these multiplets with temperature classification is fairly satisfactory, but inspection of the Zeeman patterns show that these data are homogeneous for some groups and quite discordant for others. W. E. G.

Structure of the Spectrum of the Neutral Chromium Atom. MIGUEL A. CATALÁN (*Anal. Fís. Quím.*, 1923, **21**, 84—125; cf. this vol., ii, 104).—A full description of the flame, arc, and spark spectra of chromium. Two classes of lines occur which may be attributed to the neutral and ionised atom, respectively. The lines of the first class can be grouped into series of triplets following Rydberg's formula with the universal constant R. They may be classified into (1) a system of series of ordinary triplets (principal, sharp, and diffuse; (2) another system similar and parallel at a distance of 4436·4; (3) a system of narrow triplets (principal and sharp); (4) lines formed by combination of the preceding systems; (5) twelve multitriplets; (6) lines formed by combination of the first three systems and system (5). The ionisation potential of chromium calculated from the term $1s$ is 6·7 volts. The first resonance potential calculated from the triplet λ 4254, 4275, 4290 is 2·89 volts. G. W. R.

Röntgen-ray Spectroscopy Applied to Metallic Compounds. KARL BECKER and FRITZ EBERT (*Z. Physik*, 1923, **16**, 165—169).—Results, as follows, have been obtained by the application of the Debye-Scherrer method of Röntgen-ray analysis, for the respective lengths of side, a, of the elementary cubical cells, and the calculated value, d, of the density of certain metals, metallic compounds, alloys, and mixed crystals: Ta, a 3·32 Å., d 16·3; Cu_2Zn_3, a 4·01 Å., d 8·17; mixed crystals containing 96·3% Mg_4Al_3 and 3·7% Al, a 4·80 Å., d 2·62; NiAl, a 2·82 Å., d 6·25; Cu_3Al, a 3·47 Å., which is smaller than the values of a (4·07 Å.) for aluminium, and (3·68 Å.) for copper, d 8·52; Ni_6W, a 3·68 Å., d 11·94. The two latter substances are most probably mixed crystals. The crystal lattice of an alloy of tungsten with 6% of nickel corresponds with the typical regular space-centred tungsten lattice. The results indicate that Bain's rule indicating the relation of the crystal symmetry of a compound to the symmetry of the components (*Chem. and Met. Eng.*, 1923, **28**, 21, 63) is not of general application. The crystal lattice of tantalum is space-centred, regular, whilst that of thallium surface-centred is tetragonal, having a 4·75 Å., c 5·40 Å. The calculated value of the density in the latter case is 11·02. J. S. G. T.

A Simple Method for the Measurement of Absorption in the Ultra-violet. CHR. WINTHER (*Z. wiss. Photochem.*, 1923, **22**, 125—130).—The method devised by the author and others (A., 1922, ii, 729) for the measurement of spectral absorption in the ultra-violet by comparison of the absorption with that of p-nitrosodimethyl-

aniline, has been improved by the use of a gauze of copper 0·15 mm. thick, as employed by Ham, Fehr, and Bitner (*J. Franklin Inst.*, 1915, **178**, 299), in place of the liquid as comparison substance. A series of exposures of a photographic plate to the light transmitted by various thicknesses of the substance being investigated is made in the usual manner, and the absorption curve determined by ascertaining a series of points, corresponding with the various thicknesses, where the light transmitted by the substance and the gauze, respectively, produced equal photographic effects on the plate. For visual observations, a plate coated with fluorescent quinine sulphate is employed. Results obtained by the application of the method to the case of a 0·002 molar solution of salicylic acid in alcohol are in close agreement with the results obtained by Henri.
J. S. G. T.

Absorption of the Ultra-violet Rays by Phosphorus and some of its Compounds. J. E. Purvis (*Proc. Camb. Phil. Soc.*, 1923, **21**, 566—567).—The absorption of ultra-violet light from a condensed cadmium spark by the vapour of phosphorus, phosphine, and phosphorus trichloride has been investigated at various temperatures. The results show that neither phosphorus nor its compounds with hydrogen or chlorine exhibit any absorption bands in the ultra-violet.
J. F. S.

The Absorption Produced by Electrically Luminescent Sodium Vapour. F. H. Newman (*Phil. Mag.*, 1923, **46**, 22—28). —The self-reversal of spectrum lines, and the absorption phenomena exhibited by a mixture of sodium and potassium vapours rendered luminescent by an electrical discharge have been investigated. The potassium lines were throughout faint compared with those of sodium, but became relatively brighter as the voltage applied to the discharge tube was decreased. Raising the temperature of the vapour from 300° to 450° caused strong self-reversal of the *D*-lines as seen through the end of the discharge tube, but no other lines exhibited self-reversal. Contrary to expectation, the intensities of the subordinate series lines were not observed to be increased in a constricted part of the discharge. This effect is attributed to self-reversal of the lines observed in the region of the constriction, where conditions favour absorption of radiation consisting of lines converging to $2p$, rather than of the *D*-lines. Self-reversal of the subordinate lines was less marked when the discharge current was reduced. Absorption of radiation corresponding with the *D*-lines alone was observed when white light passed through the luminous mixture of vapours.
J. S. G. T.

The Ultra-violet Absorption Spectrum of Glyoxal. A. Luthy (*Compt. rend.*, 1923, **176**, 1547—1548).—The absorption spectrum of a hexane solution of glyoxal, the first case in which narrow bands have been observed for an aliphatic substance, is shown in comparison with that of acetaldehyde. It is divided into three distinct regions, the first of which (between $\lambda=4613$ and $\lambda=3119$ Å.) contains seventeen narrow bands arranged in four groups,

the second one large band in the middle ultra-violet ($\lambda=2800$), and the third a large band in the extreme ultra-violet ($\lambda=1950$).

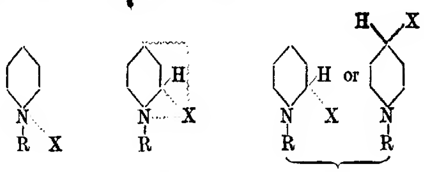
H. J. E.

The Ultra-violet Absorption Spectrum of Diacetyl. GUILLAUME C. LARDY (*Compt. rend.*, 1923, **176**, 1548—1550).—Diacetyl in hexane solution gives an absorption spectrum which differs from those obtained with other solvents in showing greater resemblance to those obtained for the vapour. Four narrow bands exist between $\lambda=4512$ and 4054 Å., and the curve rises steadily in the extreme ultra-violet. H. J. E.

The Ultra-violet Absorption Spectrum of *p*-Benzoquinone. F. W. KLINGSTEDT (*Compt. rend.*, 1923, **176**, 1550—1552; cf. two preceding abstracts).—The spectrum of *p*-benzoquinone in hexane solution is shown in comparison with that obtained by Baly (T., 1906, 89, 502). A large band occurs in the middle region ($\lambda=2790$ Å.), and one of high absorption value ($\epsilon=20,000$) in the extreme ultra-violet ($\lambda=2410$ Å.); the position and intensity of the latter are similar to those which are exhibited by all substances possessing two or three ethylenic linkings. Certain bands in the visible spectrum are also described, these being similar to those obtained in the cases of glyoxal and diacetyl, and it is pointed out that this resemblance is of importance in dealing with the theory of quinone structure.

H. J. E.

Relation between Absorption and Structure. VI. The Structure of 1-Arylpyridinium Salts and Cyclammonium Salts generally. VSEVOLOD ALEXANDROVITSCH IZMAILSKI (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 303—344).—According to the author's views on chromoisomerism (cf. A., 1915, ii, 198; 1916, i, 287), cyclammonium salts exhibit tautomerism, passing from the ammonium (I) to the carbonium (III) formulæ through an intermediate chromonium phase (II), thus



(I.) (II.) (III.)

The position of equilibrium depends on a number of factors, such as structure, presence of substituents, and physical influences (solvents, temperature, etc.). The intermediate or chromonium phase is responsible for the development of colour in these compounds; the other two forms are supposed to be colourless or faintly coloured and the compound is coloured only if these "limiting conditions" are not realised. Hydrogen and methyl in place of R in the above formulæ tend to make the nitrogen more basic and thus favour the ammonium phase; the salts are colourless,

show little absorption, and are good conductors. The introduction of the phenyl group, on the other hand, weakens the basicity of the nitrogen, and the carbonium phase is favoured; in extreme cases, the salts (such as the chlorates) are again colourless and show more or less pronounced fluorescence (cf. following abstract). The chromonium phase, or "meso-condition," is favoured by an intermediate state. The nature of the anion (X) is also important; thus, in the phenylpyridinium series, the iodides are the most strongly coloured, bromides less so, and the salts of oxygen-containing acids still less.

Rise of temperature favours the "meso" form and produces a deepening of the colour owing to the well-known tendency of the quinquevalent nitrogen to pass into the tervalent condition in these circumstances (cf. the dissociation of ammonium salts on heating). The solvent in which the heating is carried out has a considerable effect on the change; non-hydroxylic solvents with a low dielectric constant, such as chloroform, favour the production of the coloured form, whilst hydroxylic solvents inhibit the change; these solvents have been shown to affect the dissociation of quaternary ammonium salts in the same way (cf. Wedekind and Paschke, A., 1911, i, 628; von Halban, A., 1911, i, 852). Hantzsch's views of the constitution of these compounds, involving the existence of two isomeric ammonium formulæ, are criticised at length (cf. A., 1911, i, 673); the application of the theory to the chromoisomerism of *o*-quinoneimine and xanthene dyes is discussed and formulæ similar to (II), in which the anion is connected simultaneously to two or more atoms in the molecule, are devised for several of these substances.

Spectrographic measurements on a number of salts of the 1-phenylpyridinium series (cf. this vol., i, 602) were carried out. To prove the analogy of the 1-phenylpyridinium salts with the chromonium salts of triphenylcarbinol, double compounds with hydriodic acid and tin tetrabromide and tetraiodide were prepared. Phenylpyridinium iodide gives an unstable, yellow compound with hydrogen iodide; a brownish-orange compound with tin tetrabromide, and a nearly black, crystalline *compound*, $C_{11}H_{10}NI,SnI_4$, with tin tetraiodide, which was analysed. The behaviour of the pyridinium salts towards various solvents is described. G. A. R. K.

Relation between Absorption and Structure. VII. Fluorescent *N*-Arylpyridinium Salts. V. A. IZMAILSKI (*J. Russ. Phys. Chem. Soc.*, 1920, 52, 344—358).—When exposed to the light of an induction arc, a number of arylpyridinium salts exhibit fluorescence in the solid state; the phenomenon is not observed in solution, and is due almost entirely to the action of ultra-violet rays, because filtration of the light through an uviol plate or glass prevents it completely; no fluorescence is observed when the compounds are illuminated by means of a Nernst lamp. The occurrence of the phenomenon is closely bound up with the structure of the compounds, and is dependent both on the nature of the

organic radicle R attached to the nitrogen atom and that of the acid radicle X (see preceding abstract). When R=H or CH_3 no fluorescence is observed; nearly all *N*-phenyl derivatives fluoresce to some extent, and the fluorescence is greatly enhanced by the presence of a methoxy- or an ethoxy-group, less so of an hydroxyl group, in the benzene ring; the para-compounds are particularly strongly fluorescent. The methyl group, on the other hand, has an unfavourable effect, whilst halogens and nitro-groups destroy fluorescence altogether (cf. Meyer, A., 1903, ii, 706). The substitution of β-naphthyl for phenyl increases the fluorescence, whilst the introduction of α-naphthyl is unfavourable.

The introduction of hydroxyl into the pyridine nucleus itself (in the 3-position) affects fluorescence adversely; the fusion of the nucleus with an aromatic ring is favourable, but the compounds are greatly affected by the substituents, such as methyl groups, present in the pyridine ring.

The influence of the anion in these salts is considerable in the order $^-ClO_4 > ^-NO_3$ and $^-SO_4 > ^-Cl > ^-Br > ^-I$, the chlorates being the most strongly fluorescent.

Acyclic ammonium salts do not exhibit fluorescence, the tetramethyl-, phenyltrimethyl-, phenyldimethylethyl-, and phenylbenzyldimethyl-ammonium chlorates having been specially investigated. The new salts prepared include *pyridinium chlorate*, white leaflets, m. p. above 250°; *methylpyridinium chlorate*, crystals, m. p. about 130°; *phenyldimethylethylammonium chlorate*, colourless needles, m. p. indefinite, about 200°; *phenyltrimethylammonium chlorate*, yellow powder, m. p. 130—150°. A list is given of the 103 compounds examined.

From the above facts it is concluded that ammonium salts and pyridinium salts having an ammonium structure do not exhibit fluorescence; the fluorescence of dihydropyridine derivatives (cf. Ley and Engelhardt, A., 1908, ii, 911; 1910, ii, 813), of such compounds as maleinimide and succinimide and of heterocyclic compounds existing in a carbonium phase point to the latter possessing the function of a fluorophore in the cases under discussion. The phenyl group attached to nitrogen may share in this function, but it is not sufficient to produce fluorescence if the nitrogen is quinquevalent, as in the acyclic ammonium salts described above; whilst tervalent nitrogen appears to function as an auxophore. In accordance with this, conditions favouring the basic function of the nitrogen and, consequently, the ammonium form of the salt are unfavourable to fluorescence, whilst conditions diminishing the basicity of the nitrogen have the reverse effect. G. A. R. K.

Investigations on the Dependence of Rotatory Power on Chemical Constitution. XX. The Rational Study of Optical Properties including Refraction. HAROLD HUNTER (T., 1923, 123, 1671—1682).

The Natural Optical Activity of Regular Crystals of Sodium Chlorate and Sodium Bromate. CARL HERMANN (*Z. Physik*, 1923, 16, 103—134).—Born's theory of the optics of crystals, based

on dynamical considerations applied to the crystal lattice (*ibid.*, 1922, 8, 390), is employed to deduce expressions, in the form of power series, for the respective optical rotatory powers of sodium chlorate and sodium bromate, crystals characterised by being regular and optically isotropic, which are optically inactive when in solution or molten. Observed and calculated values of optical rotatory power for wave-lengths between 4×10^{-5} and 8×10^{-5} cm. are in close agreement in the case of sodium bromate. Complete agreement, at least for the long wave-length region, is obtainable by a slight displacement of the electronic centre of mass. Differences shown in the region of short wave-lengths indicate that the assumptions made in the theory, viz., that the electrons and corresponding anion may be regarded as concentrated in respective points, is unjustified in the region of resonant frequencies. In the case of sodium chlorate, calculated values of the rotatory power are approximately only one-half the experimental values. This result indicates the necessity for considerable alteration in the structure of the lattice model employed in developing the theory, possibly effected by a displacement of the centre of mass of the electrons, a procedure possible only with Vegard's model (this vol., ii, 162) and not with those of Kolkmeyer, Bijvoet, and Karssen (A., 1921, ii, 200) or Dickinson and Goodhue (A., 1922, ii, 145). J. S. G. T.

The Behaviour of the More Important Carbohydrates (Dextrose, Galactose, Lævulose, Mannose, Maltose, Lactose, Sucrose) in Strong Acid, Alkali, Sulphite, and Hydrogen Sulphite Solutions. II. The Mutarotation and Rotation of Carbohydrates under the Action of Strong Acids. B. BLEYER and H. SCHMIDT (*Biochem. Z.*, 1923, **138**, 119—141).—Arising out of the authors' work on the hydrolysis of lactose by strong acids (this vol., ii, 306), the effects on the specific rotation of various mono- and di-saccharides of concentrations of sulphuric acid up to 28*N* are investigated. The changes of $[\alpha]_D$ shown by such sugars as dextrose and galactose are classified as primary and secondary. The former type of change is a gradual rise of equilibrium $[\alpha]_D$ with increasing concentration of acid up to 22*N*. For any given concentration up to this limit, the $[\alpha]_D$ initially reached is constant. The secondary change, shown in acid concentrations of 24*N* and above, is a slow upward change of rotation from the initial equilibrium value, which is ascribed to a gradual condensation of the monosaccharide to form disaccharides (maltose, *iso*maltose, galactobiose). Lactose shows the same type of primary change as dextrose and galactose; hydrolysis begins at 18*N*. Maltose is exceptional in that the variation of $[\alpha]_D$ with acid concentration is much less marked than in the case of the other sugars mentioned, a slight fall up to 12*N* and a rise from 12*N* to 22*N* being observed. In 24*N* acid maltose reaches the same final equilibrium as is attained by dextrose in the same acid concentration. Mannose in 24*N*-H_2SO_4 shows an initial equilibrium lævorotation (cf. the equilibrium dextrorotation in water) which slowly changes to dextrorotation. It is suggested that this is again due to disaccharide formation.

Lævulose shows an increase of $[\alpha]_D$ up to $16N$ acid; above this concentration, a fall in $[\alpha]_D$ associated with decomposition is observed. Sucrose in $28N$-H_2SO_4 at 15° is immediately hydrolysed. The observations are extended to other acids (hydrochloric, nitric, perchloric, formic, and acetic) with results similar to those already recorded. In its behaviour towards concentrated nitric acid (d=1·38) lævulose differs from the other sugars, which show rises in $[\alpha]_D$ followed by falls and the formation of coloured decomposition products. Lævulose shows a continuous slow fall in $[\alpha]_D$ to an equilibrium value which corresponds with the formation of a colourless oxidation product. This has not been identified, but it is suggested that it may be of the type of β-ketogluconic acid.

It is concluded that these results do not accord with the existing theories of mutarotation (Lippmann, Hudson, Fischer, and Tollens), and a new theory is deduced which involves the fusion of the Lippmann and Hudson theories with the "hydration" theories.

J. P.

Rotation Dispersion. I. Lifschitz (*Z. physikal. Chem.*, 1923, 105, 27—54).—Rotation of the plane of polarised light and rotation dispersion is discussed, and it is shown that the existence of optical activity depends on the presence of at least four coupled electrons, which possess only axial symmetry. This system may be carried by a single atom or by several atoms of the molecule, and in the first case the atom carrying the asymmetric electron system is known as the asymmetric atom. A close relationship exists between absorption of light and the Cotton effect. The Cotton effect is to be expected in those bands which may be attributed to the asymmetric or, better expressed, axial symmetric electron systems. An optically active molecule may contain several such electron systems, and consequently the rotation dispersion can, because of internal superposition, exhibit an abnormal character. The relationship between rotation dispersion and absorption and circular dichroism, respectively, in the absorption bands of active substances can furnish valuable information in connexion with analysis of spectra and in the consideration of stereochemical problems. The rotation dispersion of a large number of heavy metal complex derivatives and organic substances has been investigated, and the results have been discussed in connexion with spectroscopic, photochemical, and stereochemical data. The specific rotation of the bivalent cobalt, nickel, and uranyl derivatives of d-hydroxymethylenecamphor and nitrocamphor, the tervalent cobalt, chromium, and aluminium salts of d-hydroxymethylenecamphor, d-hydroxymethylenecamphor, d-camphorquinone, oximinocamphor, and camphorquinonephenylhydrazone has been measured in various solvents and with light of various wave-lengths. The results are presented in tabulated form and also as curves. In the formation of resolvable complexes from active materials, in many cases partial asymmetric syntheses are achieved, the significance and nature of which are discussed.

J. F. S.

The Theory of Photochemical Reactions. W. NERNST and W. NODDACK (*Sitzungsber. Akad. Wiss. Berlin*, 1923, **15**, 110—115).—Various typical photochemical reactions are briefly reviewed, and the authors conclude that whilst in purely photochemical processes light is absorbed in quanta, experimental verification of this fact is possible only for radiation confined within a restricted spectral region, and when the reaction occurs under relatively simple conditions, as the photochemical process is, in general, accompanied by a dark reaction which very materially affects the amount of substance transformed. General thermodynamic considerations indicate, as pointed out by Warburg (A., 1920, ii, 210) that the quantum relation $Q=Nh\nu$ cannot apply in the case of a photochemical process effected by radiation of such long wavelength that the quanta are too small to render the reaction possible. In the case of photochemical processes effected by radiation characterised by very large quanta, *e.g.*, the effect of Röntgen rays on a photographic plate, the amount of substance transformed is very much larger than that calculated from the quantum relation $Q=Nh\nu$, and in all such cases the relation must be replaced by the equation $Q=Nq$, where q denotes the energy of atomic dissociation of the molecule concerned. The photochemical law of equivalence may be shown to hold when the absorbed quantum of energy is not greatly different from the energy necessary to initiate the chemical process concerned and when the photochemical process proper is not accompanied by secondary reactions.

J. S. G. T.

Investigation of the Application of the Photochemical Equivalence Law to Dry [Photographic] Plates. J. EGGERT and W. NODDACK (*Sitzungsber. Akad. Wiss. Berlin*, 1923, **15**, 116—122).—In continuation of previous work (*ibid.*, 1921, **13**, 631), the authors have shown that the photochemical equivalence law is applicable to the process occurring when a silver bromide gelatin emulsion is illuminated with radiations of respective wavelengths 436, 405, and 365 $\mu\mu$, provided the incident radiation is not too intense.

J. S. G. T.

Action of Traces of Impurities on the Photochemical Synthesis of Carbonyl Chloride. J. CATHALA (*Bull. Soc. chim.*, 1923, [iv], **33**, 576—581).—An apparatus for the study of the photochemical synthesis of carbonyl chloride is described consisting essentially of an ampoule containing the liquefied gas, which is allowed to evaporate into a graduated reservoir charged with mercury. A measured volume is displaced by the mercury into a quartz vessel heated to about 850° in an electric furnace, where the carbonyl chloride is completely dissociated and passes after cooling into a jacketed transparent quartz vessel illuminated by the light of a mercury vapour lamp. The product is analysed by estimations of the free and the combined chlorine. The preliminary experiments revealed considerable variations in the yield under similar outward conditions, increasing yields of carbonyl chloride being obtained from the carbon monoxide and chlorine

derived from the dissociation of the vapours evolved from the later fractions of liquefied carbonyl chloride in the ampoule. The introduction of a small quantity of air into the gases at the later stage once again caused a lowering of the yield, but this could not be attributed to the effect of oxygen in this case, as this gas would be eliminated as carbon dioxide in the furnace, and it is therefore the carbon dioxide formed from carbon monoxide and the oxygen dissolved in the liquefied carbonyl chloride which apparently causes the observed retarding action on the photochemical synthesis.

G. F. M.

Photochemical Studies. I. Photochemical Decomposition of solid Oxalic Acid. W. ALBERT NOYES, jun., and A. B. KOUPERMAN (*J. Amer. Chem. Soc.*, 1923, **45**, 1398—1400).—The photochemical decomposition of anhydrous oxalic acid, hydrated oxalic acid, a saturated solution of oxalic acid in contact with the solid, and formic acid has been investigated. As sources of illumination were used a carbon arc which gave light down to 250 $\mu\mu$, a carbon arc in which the electrodes had been previously soaked in salt solutions, which extended the range to 220 $\mu\mu$, a mercury lamp with a quartz window giving light to 185 $\mu\mu$, and a mercury lamp with a fluorite window giving light to 100 $\mu\mu$. The results show that anhydrous oxalic acid is decomposed by ultra-violet light of wave-lengths shorter than 250 $\mu\mu$. The rate of decomposition is greater for shorter wave-lengths. The rate of decomposition is much increased by the presence of water, but there is a long induction period which is less when water is present than when it is absent. In the case of formic acid, the induction period is small. Since water vapour is one of the products of decomposition, the action may be autocatalytic, and this may be the explanation of the induction period. Other possible explanations of the induction period are that it may be due to the slow production of formic acid, this being then rapidly decomposed. In this case, the rate of reaction would not reach a maximum until the rate of production of formic acid became constant, or the induction period may be due to the slow rate of diffusion of the products of decomposition out of the solid and from the surface. These various possibilities are discussed. After the induction period, the rate of reaction is constant. The wave-length necessary to decompose the solid acid does not agree with that calculated from Perrin's formula, based on a rough determination of the temperature coefficient of the rate of thermal decomposition. J. F. S.

An Application of the Anti-oxygenising Power of Phenols: Increase in Fastness to Light of Dyes on Fibre. ALFRED GILLET and FERNAND GIOT (*Compt. rend.*, 1923, **176**, 1558—1560; cf. this vol., i, 675).—Treatment of fabrics with dyes which are not fast to light and subsequently with diphenols and other anti-oxygenisers shows that these exert a protective action against light whether they enter into the molecular structure or not. Azo-dyes on cotton and wool and some acid colours such as eosin are protected, but this protection does not extend to nitro-dyes; the

suggestion of auto-oxidation is made with regard to the latter. Fading of triphenylmethane dyes of all types seems to be, not oxidation, but another type of reaction. Basic colours are not protected, quinol in alkaline solution even accelerates the change. In some cases, a considerable excess of the diphenol (10 mols. to 1 mol. of dye) is required to give definite protection. [Cf. *J.S.C.I.*, 1923, Aug.] H. J. E.

Photochemical Transformation of Fluorescent Dye Solutions. PETER PRINGSHEIM (*Z. Physik*, 1923, **16**, 71—76).—In reply to Weigert's criticism (A., 1922, ii, 681) of the author's previous work indicating that the photochemical law of equivalence does not apply when part of the absorbed radiation is re-emitted as fluorescence, the author shows that, in the case of an alkaline aqueous solution of eosin, which ordinarily is only slightly sensitive to photochemical change, and becomes extremely sensitive when a little ethyl alcohol is added to the solution, identical light-absorbing and fluorescent properties are possessed by both forms of solution. In the extremely sensitive solution, fluorescence and chemical reaction are both excited by light confined to the same spectral region, and can both be produced by monochromatic radiation. J. S. G. T.

Photoelectric Conduction and Chemical Combination. B. GUDDEN and R. POHL (*Z. Physik*, 1923, **16**, 42—45).—The photoelectric properties of certain compounds, viz., carbonates, halides, oxides, sulphides, etc., of metals such as mercury, silver, cadmium, etc., are correlated with various physico-chemical properties of these substances, viz., colour, lattice energy, volatility, solubility, etc., which are attributed by Fajans (*Naturwiss.*, 1923, **11**, 165) to a distortion of the shell of the anionic electrons by the kations. J. S. G. T.

Radioactive Constants up to 1923. STEFAN MEYER (*Jahrb. Radioaktiv. Elektronik*, 1923, **19**, 334—344).—The constants given in 1920 (A., 1921, ii, 235) are brought up to date. W. E. G.

Characteristic Röntgen Radiation of the First [Lighter] Elements. J. HOLTSMARK (*Physikal. Z.*, 1923, **24**, 225—230).—In continuation of previous work (A., 1922, ii, 543), the author has investigated photoelectrically the limiting values of potential necessary for the excitation of K-radiation in lithium and glucinum, respectively. The value found for lithium is 52·6 volts, and for glucinum a provisional value, 95 ± 5 volts, is given. In the case of lithium, a linear relation, differing according as the value of the exciting potential was respectively above or below the critical value, was established between the ratio of the photoelectric effect to the intensity of the exciting cathode rays and the exciting potential. A similar discontinuity was not observed in the case of glucinum. Available data relating to limiting potentials necessary for exciting K-radiation in the case of the lighter elements of atomic number 1—11 are tabulated. A linear relationship exists between the square root of the critical exciting potential

and the atomic number (z) of the corresponding elements for values of z equal to 2, 3, 4, and 5. The relationship in the case of the remaining elements is different, and the cause of this difference is briefly discussed in the light of Bohr's theory of atomic structure. J. S. G. T.

The Quantitative Measurement of Radium Emanation by the α-Radiation. Corrections for Pressure and for the Nature of the Gaseous Mixture. ADOLPHE LEPAPE (*Compt. rend.*, 1923, **176**, 1613—1616).—In measuring the radium emanation used for experiments on the ionisation of gases, certain corrections should be made. When the pressure is less than 720 mm., or if any considerable percentage of carbon dioxide is present, the ionising effect of the emanation is sensibly changed. The dimensions of the condenser should also be taken into account. Results of experiments in which these factors vary over a wide range are given. H. J. E.

The Constant of Polonium. (MLLE) ST. MARACINEANU (*Compt. rend.*, 1923, **176**, 1879—1881).—As the result of a large number of experiments, the author obtains the value 139·5 days for the half-change period, the radioactive constant, λ, being $4{\cdot}96\times10^{-3}$ (day)$^{-1}$. The best results were obtained with polonium on glass, with or without a screen. The examination of radioactive material deposited on metallic surfaces is not recommended. E. E. T.

The Collision Area of Molecules of the Rare Gases towards Slow Electrons. CARL RAMSAUER (*Jahrb. Radioaktiv. Elektronik*, 1923, **19**, 345—354).—Measurements of the collision areas of molecules of the rare gases have shown that these gases behave in a very different manner from hydrogen and nitrogen. As the velocity of the electron falls, the area of nitrogen and hydrogen molecules increases to a constant value which does not differ widely from that deduced from the kinetic theory. On the other hand, the collision area of the molecules of the rare gases at first increases to a maximum and then decreases rapidly as the velocity of the electron decreases. For argon, krypton, and xenon, the collision area at the maximum is four or five times, and at 0·75 V is one-seventh of that derived from the kinetic theory. These gases are practically transparent to slow-moving electrons. These results are at variance with the electricity laws, which require that the collision area should approach infinity as the electron velocity approaches zero. W. E. G.

Dielectric Constants of Colloidal Solutions. IV. J. ERRERA (*Kolloid Z.*, 1923, **32**, 373—376; cf. A., 1922, ii, 694; this vol., ii, 225).—A continuation of previous work. The dependence of the dielectric constant of vanadium pentoxide sols on the potential difference with different wave-lengths has been investigated and it is shown that the dielectric constant increases with increasing

potential. The dependence of the dielectric constant of vanadium pentoxide sols on the frequency of the alternating current is expressed generally by a curve which is made up of four sections, a concave slowly rising section, a rapidly rising straight line, a saturation section, and a slowly rising section. The experimental results have been briefly discussed in connexion with the dipole theory. J. F. S.

Calibration of Cells for Conductivity Measurements. II. Intercomparison of Cell Constants. HENRY C. PARKER (*J. Amer. Chem. Soc.*, 1923, **45**, 1366—1379; cf. this vol., ii, 6).—A new method is described for the intercomparison of cell constants over a large range of concentration and the results of several series of such comparisons are given. The range of concentrations through which the intercomparisons were made is twenty-five times as great as that used previously. The effect of platinising and the disposition of the electrodes on a cell constant is shown by the intercomparison curves. It is indicated that there is a gradual transition in the shape of the curve as the electrodes are placed farther apart, the farthest apart giving a curve showing the most nearly constant value. None of the electrodes compared give what may be considered as a fixed value for the derived cell constant. A new effect, similar in some respects to polarisation, is found to occur at high dilutions with all types of cells used in the present work. This effect is shown to amount to at least 0·33% at moderate concentrations, in the case of one type of electrode which has been used in many accurate conductivity measurements. Correction of the existing conductivity data for this effect would tend to increase the values of the equivalent conductivity at the higher dilutions. The limiting values would probably be affected to a considerable extent, the values of the calculated degree of ionisation being reduced in like proportion. A theory to account for this effect, at high dilutions, is put forward, which assumes the presence of an adsorbed layer in contact with the electrodes. The correction for the resistance of this layer is assumed to be positive or negative, according to whether the adsorbed layer contains an excess or a deficiency of the conducting material. J. F. S.

Membrane Potentials in the Donnan Equilibrium. DAVID I. HITCHCOCK (*J. Gen. Physiol.*, 1923, **5**, 661—663).—It is pointed out that although Loeb's views on the rôle of Donnan's theory in regulating the properties of proteins necessarily leads to results in agreement with the second law of thermodynamics, his work constitutes a distinct advance. Hill, in his criticism (this vol., ii, 221), has offered no other explanation of the facts. W. O. K.

Phenomenon of Electrical Supertension. III. A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **26**, 259—265; cf. A., **1919**, ii, 91, 387).—A theoretical paper in which the electrical supertension of a palladium or platinum electrode is considered

when the metal is functioning as a cathode. The equilibria are considered on the basis of the theory of allotropy. J. F. S.

Metallised Electrodes from Porous Clay and the Simplest Form of the Acid-Alkali Cell. K. A. HOFMANN (*Ber.*, 1923, 56, [*B*], 1456—1463).—The behaviour of electrodes made of tubes of porous clay impregnated with platinum, palladium, or iridium has been examined. The electrodes are moistened with 2*N*-sodium hydroxide solution or 2*N*-sulphuric acid and partly immersed in sulphuric acid or sodium hydroxide solution, their upper portions being surrounded by hydrogen or hydrogen and oxygen, respectively. It is found that such electrodes when placed in the oppositely active electrolyte or in a neutral salt solution render the surrounding gas as active as if they were not immersed in the electrolyte but in the moistening acid or alkali. It follows, therefore, that the electrically active layer must lie at the zone of contact of the gas and the moistening acid or alkali, that is, at the surface of the tube above the liquid. Peculiar properties of the impregnated electrodes are (i) the unexpected stability of the sulphuric acid used in moistening the tubes towards the neutralising action of the sodium hydroxide with which the lower end is surrounded, (ii) the much smaller but still considerable stability of sodium hydroxide towards sulphuric acid under similar conditions, (iii) the increase in potential after the current has been allowed to flow, and (iv) the slower attainment of the highest potential by electrodes moistened with sulphuric acid than by those wetted with sodium hydroxide. A probable explanation of these peculiarities is found in the protective action of the layer of neutral salt produced within the tube. H. W.

Intermittent Current Electrolysis. I. The Influence of Intermittent Current on Overvoltage. SAMUEL GLASSTONE (T., 1923, **123**, 1745—1750).

Electrolytic Conduction: Sequel to an Attempt (1886) to Apply a Theory of Residual Affinity. HENRY E. ARMSTRONG (*Proc. Roy. Soc.*, 1923, [*A*], **103**, 619—621).—The theory of residual affinity advanced by the author in explanation of the phenomena of electrolytic conduction (*ibid.*, 1886, **40**, 268) is illustrated more especially by reference to the work of Tubandt (A., 1921, ii, 426) on the electrical conducting properties of the heated solid halides of silver and lead. In the case of silver iodide, the primarily active unit is AgI, whilst in lead chloride the active unit is $PbCl_2$. By assuming one or more of these primary units to be distributed at each electrode and that a circuit is formed by these molecules being coupled with complex molecules which differ in structure in the two cases, the author shows how, in the case of silver iodide, silver is deposited at one electrode and withdrawn from the other, while in the lead halides, the halogen is abandoned to the one electrode and taken from the other, results which agree with those obtained by Tubandt. A similar interpretation may equally be applied to the process of electrolysis of aqueous solutions (this vol., ii, 542). J. S. G. T.

A New Method to Determine the Hydration of Ions. The Hydration of the Lithium-ion. G. BABAROVSKÝ (*Rec. trav. chim.*, 1923, **42**, 533—534; cf. this vol., ii, 288).—Corrects some arithmetical errors in the preceding paper. F. A. M.

Ionisation of Alcohols. ROGER J. WILLIAMS and R. W. TRUESDAIL (*J. Amer. Chem. Soc.*, 1923, **45**, 1348—1353).—An attempt to determine the nature and the extent of the ionisation of ethyl alcohol has been made by investigation of the point of equilibrium of the reaction $EtOH+NaOH \rightleftharpoons H_2O+EtONa$. The method of determining the amount of water formed consisted in shaking a known amount of the mixture with a known weight of granules of calcium carbide for a definite length of time so that only about 4% of the water was used up. The calcium in suspension as hydroxide was determined nephelometrically and by comparison of this with the values obtained by the action of calcium carbide on samples of alcohol containing known amounts of water the amount of water actually present in the reaction mixture was ascertained. The results for the degree of ionisation into hydrogen- and ethoxide-ions are, from the nature of the method, too high, but, despite this, they appear to confirm the much more accurate value found by Danner and Hildebrand (this vol., ii, 166, 117). Assuming that esterification is a neutralisation reaction, the degree of ionisation of alcohol into ethyl- and hydroxyl-ions is shown by calculation to be zero. The reaction of methyl alcohol with magnesium nitride, calcium hydride, and calcium carbide, respectively, has been investigated, and it is shown that in each case the alcohol reacts as a weak acid, and that there is no evidence to indicate that it ionises in any other way than as a weak acid, namely, $CH_3{\cdot}OH \rightleftharpoons CH_3{\cdot}O'+H^{\cdot}$. With magnesium nitride, the reaction is $6CH_3{\cdot}OH+Mg_3N_2 \rightarrow 3Mg(O{\cdot}CH_3)_2+2NH_3$, with calcium hydride, $CH_3{\cdot}OH+CaH_2=(CH_3{\cdot}O)_2Ca+H_2$, and with calcium carbide $2CH_3{\cdot}OH+CaC_2=Ca(O{\cdot}CH_3)_2+C_2H_2$. J. F. S.

Atomic Heats of Cadmium and Tin at Low Temperatures. WORTH H. RODEBUSH (*J. Amer. Chem. Soc.*, 1923, **45**, 1413—1416). —The atomic heats of cadmium and tin have been measured by the same method as was employed by Eastman and Rodebush for similar determinations of the alkali metals (A., 1918, ii, 149). The apparatus was of the same kind, but constructed of metal. The present measurements extend over the range 70—100° K. and are sufficiently accurate for use in fixing the curves for the metals over the temperature range 0—298° K. The following values for C_p are recorded: cadmium, 69·66°, 4·67; 72·40°, 4·74; 77·56°, 4·88; 80·09°, 4·96; 85·06°, 5·04; 87·70°, 5·11; 89·91°, 5·15; 94·70°, 5·23; 97·08°, 5·26; 99·37°, 5·31; 298°, 6·25; tin, 69·93°, 4·57; 72·39°, 4·64; 77·71°, 4·83; 84·00°, 4·98; 88·90°, 5·07; 93·56°, 5·17; 96·21°, 5·26; 101·00°, 5·34; 298°, 6·50. J. F. S.

Chemical Constants of Diatomic Molecules. R. R. S. COX (*Proc. Camb. Phil. Soc.*, 1923, **21**, 541—551).—A theoretical discussion in which it appears that no certain conclusion as to the

chemical constants of diatomic molecules can at present be drawn. It seems quite possible that the discordance between the value found and the theoretical value may have a theoretical basis; but this cannot be asserted until further experimental data are available. Accurate and numerous measurements of p and K_p, further information as to the specific heat of the vapour and solid at low temperatures, and measurements of the band spectra are necessary before much further progress can be made. J. F. S.

Heat Capacities and Entropies of Diatomic and Polyatomic Gases. H. C. UREY (*J. Amer. Chem. Soc.*, 1923, **45**, 1445—1455). —A theoretical paper in which the entropy constant for diatomic gases having no vibrational energy is evaluated. The entropy of hydrogen (29·25), nitrogen (45·59), hydrogen fluoride (39·84), hydrogen chloride (42·95), hydrogen bromide (45·79), carbon monoxide (45·6), and nitric oxide (45·3) have been calculated from equations deduced in the paper and the values given in brackets found for 25°. These values have been compared, wherever possible, with experimental entropy determinations, and in most cases an exceptionally good agreement has been found. The moments of inertia of oxygen (41×10^{-40}), hydrogen iodide (4×10^{-40}), and chlorine (109×10^{-40}) have been calculated from their observed entropies, and attention is directed to the probability that oxygen and possibly nitric oxide do not follow the equation deduced. The values for the moment of inertia at 25° are given in brackets. The entropy equation for diatomic gases which possess vibrational heat capacity is discussed. The constant for the entropy equation of gases the molecules of which have tetrahedral symmetry has been obtained and the dimensions of the methane molecule are calculated. Using this equation, $S=R\log_e T^{3/2}M^{3/2}V-11\cdot39+3/2R\log_e T+R\log_e I+99\cdot14$, and inserting the value $I=2\cdot232\times10^{-41}$ gives the entropy of methane as 34·25. J. F. S.

The Properties of Saturated Fluids in the Region of the Critical Point. J. E. VERSCHAFFELT (*J. Phys. Radium*, 1923, **4**, 158—169).—Assuming that the conditions of continuity are satisfied at the critical point, the characteristic equation of a saturated fluid in this region is deduced by expanding p, the pressure, in a series of ascending powers of $v-v_c$ and of $T-T_c$, v_c and T_c being, respectively, the critical volume and critical temperature of the fluid. The values of the constants in the expansion are determined by applying thermodynamic principles. The v,T saturation curve is, on these assumptions, shown to approximate to a parabola of the second degree in the region of the critical point. The author considers that experimental evidence is in accord with the existence of an analytical discontinuity at the critical point in the case of the critical isothermal, and shows that, under these conditions, the saturation vT curve consists of two branches, similarly directed, of a parabola of the third degree. Moreover, it is considered that the existence of the analytical discontinuity referred to is not in discord with the physical continuity of the liquid and gaseous states. J. S. G. T.

The Thermodynamics of the Formation of Mixed Crystals. K. F. Herzfeld (*Z. Physik*, 1923, **16**, 84—99).—The formula deduced by Grimm and Herzfeld for the heat of formation of mixed crystals (*ibid.*, 77) from consideration of the energy associated with the respective crystal lattices, is applied to obtain thermodynamic formulæ relating more especially to the entropy, miscibility, and the critical temperature of separation into components, in the case of mixed crystals. Reference is also made to the absorption of salts by crystals at low temperatures, and the precipitation of mixed crystals from solutions. The theoretical results are compared with experimental results in the cases of the pairs of salts, KCl,NaCl; KF,RbF; and KBr,KI. J. S. G. T.

Cryoscopic Investigations of some Solutions in Bromine. Wladimir Finkelstein (*Z. physikal. Chem*, 1923, **105**, 10—26).—The cryoscopic constant for highly purified bromine has been determined by measuring the depression of the freezing point of bromine brought about by dissolving carbon tetrachloride in it. Assuming that carbon tetrachloride is unimolecular and has the molecular weight 153·84, the cryoscopic constant is found to be 83·12. The value obtained from van't Hoff's formula, using 16·185 as the latent heat of fusion of bromine and $-7·32°$ as the freezing point, is 86·35. The depression of the freezing point of bromine brought about by arsenic tribromide, sulphur monobromide, aluminium tribromide, and tribromoacetic acid has been determined for several concentrations in each case. The results show that the substances arsenic tribromide, sulphur monobromide, and carbon tetrachloride, which do not conduct an electric current in bromine solution, have molecular weights strictly the same as the theoretical values, whilst aluminium tribromide and tribromoacetic acid which do conduct an electric current in bromine solution have molecular weights twice as large as the theoretical value, and the polymerisation constant in these cases is the same for all concentrations. Further determinations were carried out with phosphorus pentabromide, acetamide, and antimony tribromide; all these substances are conductors of electricity when dissolved in bromine, and in consequence of solvation and polymerisation they form complexes which increase in complexity with increasing concentration. In the case of acetamide, the curve between molecular weight and concentration shows a definite maximum which lies at about 2%, and it is at this point it is suggested that the maximum complexity lies, or at least the influence of dissociation is equal to that of complex formation, and at higher concentration than 2% the dissociation is increasingly greater than the complex formation. The electrical conductivity of the solutions examined is closely connected with the formation of complicated complex molecules. J. F. S.

The Investigation of Double Salts in Solution by Ebullioscopic Methods. F. Bourion and E. Rouyer (*Compt. rend.*, 1923, **176**, 1708—1710).—A mathematical investigation of the law of mixtures as applied to the investigation of double salts in solution

by the method of continuous variations when applied to ebullioscopic measurements (this vol., ii, 57). G. F. M.

A Method for the Determination of Molecular Weights in Aqueous Solution. KASIMIR JABLCZYŃSKI (*I^{szy} Zjazd Chemików Polskich*, 1923, 19).—A method for the determination of molecular weights in aqueous solution is described, depending on the difference in the rates of evaporation of a given solution and of water under parallel conditions. R. T.

Sublimation of Plant and Animal Products. ARNO VIEHAEVER (*J. Assoc. Off. Afric. Chem.*, 1923, 6, 473—481).—Apparatus is described for the ready sublimation of large or small quantities of material. Observations of crystalline form, melting and subliming points, etc., may be made directly with the microscope. A. G. P.

The Principle of a General Method of Determining the Calorific Capacity of Solids and Liquids. Application to the Determination of the Water Value of Calorimetric Bombs. CHARLES MOUREU, CHARLES DUFRAISSE, and PH. LANDRIEU (*Compt. rend.*, 1923, 176, 1513—1515).—The essential feature of the method is the use of two separate resistances, identical in design, material, and electrical value, which are placed in two similar calorimeters. The resistances are set up in series and connected with a source of current. In one calorimeter the solid is placed in a known mass of distilled water; in the other there is a weighed amount of water. A thermometer is placed in each calorimeter, these two thermometers being standardised against each other. The method eliminates errors due to inaccuracy of the thermometer and obviates the use of the mechanical equivalent of heat as a factor in calculation. Moreover, no electrical measurements are necessary while the current is passing. Experiments with this form of apparatus are in progress. H. J. E.

The Heat of Formation of Solid Solutions. G. BRUNI (*Bull. Soc. chim.*, 1923, [iv], 33, 696—697).—The author criticises Landrieu's results (A., 1922, i, 808), and especially his conclusion that solid solutions are differentiated from mixed crystals by the exceedingly small heats of formation of the latter. Previously published evidence is adduced in support of the present author's contention (cf. following abstract). H. H.

[The Heat of Formation of Solid Solutions.] PH. LANDRIEU (*Bull. Soc. chim.*, 1923, [iv], 33, 697—699).—A reply to Bruni (cf. preceding abstract). The author maintains his previous contention and asserts that his critic has fallen into error by quoting thermal data obtained at temperatures at which the crystals studied are unstable. H. H.

The Heats of Formation of Quinonoid Structures. ZOFJA BŁASZKOWSKA (*I^{szy} Zjazd Chemików Polskich*, 1923, 27—28).—The reactions of the formation of quinonechloroimine from *p*-amino-

phenol, and of quinonedichlorodi-imine from *p*-phenylenediamine are investigated thermochemically. From these and other results, it is concluded that the heat of formation of the quinonoid structure is greater for naphthalene than for benzene compounds, and less for diphenyl derivatives. The introduction into the nucleus of positive groups increases the heat effect. R. T.

Thermochemical Researches on the Diazotisation of Aminophenols. ZOFJA BŁASZKOWSKA (*I^{szy} Zjazd Chemików Polskich*, 1923, 28—29).—The heat effects of the action on picramic acid and *p*-aminophenol of excess of hydrochloric acid, excess of sodium hydroxide, of diazotisation, and of sodium hydroxide on the product of the latter, and of the formation of the compound with β-naphthol are measured. These results show that the reactions of picramic acid, and in particular that of diazotisation, take a course different from that with the majority of amines, probably a quinonediazide being produced. *p*-Aminophenol, on the other hand, behaves normally. R. T.

Heat of Solution of Thallium in Dilute Thallium Amalgams. THEODORE W. RICHARDS and CHARLES P. SMYTH (*J. Amer. Chem. Soc.*, 1923, **45**, 1455—1460).—The heat of solution of thallium in thallium amalgams of 0·0—11·17% thallium has been determined by the adiabatic method. The following values of the heat of solution in joules at 20° of 1 g.-atom of thallium in amalgams of the composition stated are recorded: 0·92%, 2706; 2·49%, 2265; 3·81%, 1917; 5·21%, 1590; 6·89%, 1075; 8·76%, 486; 10·43%, 45; 11·81%, −234. These values are compared with those obtained by Richards and Daniels for concentrated amalgams, and found to be consistent with them (A., 1920, ii, 34). A short extrapolation of the composition–heat of solution curve above 0·92% gives a value for the heat of solution of thallium in an infinite quantity of mercury of 2970 joules, a value which is in fair agreement with 3220 joules, the value obtained by Lewis and Randall (A., 1921, ii, 241) by calculation from the *E.M.F.* measurements of Richards and Daniels (*loc. cit.*) of thallium amalgam concentration cells. J. F. S.

Calorimetry of High Explosives. (SIR) R. ROBERTSON and W. E. GARNER (*Proc. Roy. Soc.*, 1923, [*A*], **103**, 539—556).—A form of calorimetric bomb designed for measuring the heat developed and the volume of the gases produced by the detonation of high explosives under standardised conditions is described. The charge of explosive was compressed to a uniform density throughout and the explosion was initiated by a standard impulse from a fulminating explosive. The following values were found for the heats of detonation of the respective high explosives: trinitrophenol, 916; trinitrotoluene, 926; and amatol, 80/20 (*i.e.*, 80 parts of ammonium nitrate to 20 parts of T.N.T.), 992 cals. per g., the water in each case being considered as gaseous. The corresponding mean values of the total volumes of gases evolved per g. of explosive were: 727, 711,

and 907 c.c., the values differing slightly according as the explosion was initiated by fulminate or azide. In the case of an explosive, *e.g.*, amatol, the composition of which permits of complete combustion, the heat of detonation and volume of gases evolved agree with those deduced theoretically. The products of detonation of high explosives in a vacuum include carbon dioxide and monoxide, water, methane, acetylene, ammonia, hydrogen cyanide, carbon, and a trace of nitric peroxide. When the explosion is incomplete, larger volumes of nitric oxide are produced and the composition of the products is very different from that of a normal detonation. The following factors, amongst others, influence the nature of the products: density of loading in the container and bomb, completeness of detonation, and purity of explosive, nature of the initiator, and degree of tamping of the explosive. Consideration of the gaseous reactions occurring during cooling of the gases produced indicate that the formation of carbon is accompanied by an increase in the heat of detonation, and a decrease in the volume of gases liberated. Conditions determining the pressure and rate of cooling of the gases evolved also affect the heat and gases of explosion. The greater the density of loading and tamping of the explosive, the higher the pressure and the greater the deposition of carbon during the cooling process, the heat of detonation being increased and the volume of gases liberated being decreased thereby.

J. S. G. T.

Piezo-chemical Studies. XIX. Experimental Determination of the Fictitious Volume Change in Solution Equilibria. ERNST COHEN and A. L. TH. MOESVELD (*Z. physikal. Chem.*, 1923, 105, 145—154; cf. A., 1920, ii, 621).—Four methods are described for the experimental determination of the fictitious volume change in solution equilibria. Two methods are volumetric and two electrical; one method of each kind has been previously described (*loc. cit.*), but the two remaining methods are new. All four methods have been tested experimentally, and the results are recorded and the methods shown to be generally applicable.

J. F. S.

Piezo-chemical Studies. XX. Experimental Proof of Braun's Law by an Electrical Method. II. ERNST COHEN, FUSAO ISHIKAWA, and A. L. TH. MOESVELD (*Z. physikal. Chem.*, 1923, **105**, 155—172).—Braun's law can be expressed in the form $(dc/d\pi)_T : (dc/dT)_\pi = -T\Delta v/Q$, where T is the absolute experimental temperature, $(dc/d\pi)_T$ is the pressure coefficient of the solubility at constant temperature, $(dc/dT)_\pi$ is the temperature coefficient of the solubility at constant pressure, Δv is the fictitious volume change which accompanies the solution of 1 g.-mol. of a substance in an infinitely large volume of solvent at 1 atm. pressure and T°, and Q is the fictitious heat of solution. The four quantities have been determined experimentally for thallous sulphate, dc/dT by direct solubility determinations, $dc/d\pi$ also directly, and Δv and Q from *E.M.F.* measurements. The following values are recorded: $dc/dT=0{\cdot}1387$ g./degree, $dc/d\pi=0{\cdot}003377$

g./atm., $\Delta v=-0.0492$ c.c./g., $Q=14.75$ cal./g., whilst the value of Q calculated from the above equation is 14·82 cal./g. This indicates that Braun's law is true within the limits of experimental error. J. F. S.

Atomic Volumes and Solubility. ROBERT FLATT (*Helv. Chim. Acta*, 1923, 6, 698—707).—A formula was given by Bodländer (A., 1898, ii, 554) for calculating the solubility of a salt in water from its free energy of formation and the normal potentials of the ions. As for most salts the free energy is unknown, the heat of formation Q can be used and Bodländer's equation can be written $Q=E_k+nRT/mF\,.\log 1/C+Q_1+E_a$, where E_k and E_a are the normal potentials of kation and anion, n is the number of ions, m the number of valencies broken during electrolysis, F is Faraday's constant, and Q_1 is the heat of formation of the free anion when this is a complex such as SO_4. In the case of sulphates, for instance, Q_1 and E_a are unknown, but their sum is a constant for a series of sulphates and can be calculated from the solubility C of a single sulphate. The quantity so determined has been used for calculating the solubilities of a number of sparingly soluble sulphates from a knowledge of Q and E_k.

According to the theory of Born (A., 1919, ii, 214) and of Fajans (*Naturwiss.*, 1921, 9, 729), the solubility of a salt depends on the difference between the sum of the heats of hydration of the ions, Q_k+Q_a, and the lattice energy of the crystal, Q_{ka}. The low solubility of the alkaline-earth sulphates and of the perchlorates is to be attributed to the high value of the lattice energy in this isomorphous series rather than to low heats of hydration of the ions. This theory also accounts for the low solubility of lead sulphate, which has a similar crystalline form. The heats of hydration of the ions and the lattice energy are functions of the atomic volume. The values of Q_k and Q_a decrease with increasing atomic volume, and Q_{ka} attains a maximum depending on the atomic volumes of the two ions. It follows that the solubility in an isomorphous series may attain a minimum value. Thus whilst barium sulphate is less soluble than strontium sulphate it is also less soluble than barium selenate. In the alkali perchlorate series, rubidium perchlorate has the minimum solubility. The low solubility of lead sulphide and lead chloride compared with the sulphides and chlorides of the alkaline-earth metals is attributed to the two additional electrons in the outer shell of the lead atom which increase the lattice energy and are the cause of the high electrical conductivity of these compounds. E. H. R.

Viscosity of Saturated Solutions, and Solvation. KONSTANTY HRYNAKOWSKI (*I[szy] Zjazd Chemików Polskich*, 192[3], 16—17).—The viscosity of saturated solutions of various sodium and potassium salts is measured, and the degree of hydration of the solutes hence estimated. All sodium salts examined exhibit solvatation, the maximum being obtained for disodium hydrogen phosphate, and the minimum for sodium chloride. Potassium

chloride, bromide, sulphate, and chlorate do not exhibit solvation, which occurs to a small extent in solutions of the iodide and nitrate, and to a marked extent in solutions of potassium hydrogen sulphate, hydrogen carbonate, and dihydrogen phosphate. R. T.

The Structure of Thin Films. IV. Benzene Derivatives. A Condition of Stability in Unimolecular Films. N. K. Adam (*Proc. Roy. Soc.*, 1923, [*A*], **103**, 676—686).—Unimolecular films of substances, *e.g.*, *p*-hexadecylphenol, *p*-octadecylphenol, and hexadecylaniline, containing one long chain and one polar group in the para-position, orient on the surface of water like fatty acids, the phenol group forming the head of the molecule in contact with the water. Measurements of the cross section of the head (cf. A., **1922**, ii, 687) agreed with the corresponding values of the cross section of the nuclei of aromatic compounds deduced from Bragg's crystal measurements (A., 1922, ii, 128). The films show the usual phenomena of expansion to a two-dimensional vapour. Compounds such as cetyl palmitate, palmitanilide, etc., containing one polar group between two chains, or one chain and a ring, do not adhere to a water surface well enough to give measurable films, although in the expanded state such films are often more stable. The para-sulphonic acids of hexadecyl and octadecyl benzene give soap-like solutions in water. J. S. G. T.

The Structure of Thin Films. V. N. K. Adam (*Proc. Roy. Soc.*, 1923, [*A*], **103**, 687—695).—In continuation of previous work (A., 1922, ii, 687), the author has investigated the structure of thin films of certain α-bromo-acids and esters, ethyl *iso*oleate, the esters, amides, and nitriles of saturated acids, carbamide derivatives, and aldoximes. The results confirm the theory developed in the previous papers. Bromine in the α-position in the bromo-acids and esters increases the cross-section of the molecules in the films. The bromine atom increases the solubility of films of the higher fatty acids, and lowers the temperature of change from condensed to expanded films, but does not appreciably affect the properties of the expanded films. The double linking in the αβ-position relative to the CO_2Et group increases the cross-section of the molecule in the films, as in *iso*oleic acid. The transition between two forms of condensed film, as in the case of the substituted carbamides, is analogous to that between two polymorphs or allotropic modifications of solid substances. J. S. G. T.

Calculation of [Recent] Adsorption [Data]. L. Berényi (*Z. physikal. Chem.*, 1923, **105**, 55—72).—In a recent paper (A., 1920, ii, 591) the author submitted Polányi's theory of adsorption (A., 1916, ii, **474**) to a critical test, using the experimental data then available. The present paper is a continuation of this work on the recently published results of Patrick and McGavack on the adsorption of sulphur dioxide by silicic acid gels (A., 1920, ii, 417), Davidheiser and Patrick on the adsorption of ammonia by silicic acid gels (A., 1922, ii, 262), and Berl and Andress on the

adsorption of a number of vapours (methyl alcohol, ether, acetone, benzene, ethyl alcohol, and carbon tetrachloride) by activated charcoal (*Z. angew. Chem.*, 1921, **34**, 369, 377). The calculations show that Polányi's theory is fully confirmed. J. F. S.

Two Types of Adsorption. HILARY LACHS (*I*[szy] *Zjazd Chemików Polskich*, 1923, 30—31; cf. A., 1916, ii, 225).—Only substances of a similar electrical charge are able mutually to displace each other on the surface of an adsorptive substance.

R. T.

The Reciprocal Displacement of Substances Adsorbed by Precipitates. ANDRÉ CHARRIOU (*Compt. rend.*, 1923, **176**, 1890—1891; cf. this vol., ii, 261).—If precipitated aluminium hydroxide containing adsorbed chromic acid is washed with a 5% solution of a salt of a monobasic acid (chloride, bromide, iodide, nitrate, or acetate), no chromic acid is removed, and no other substance adsorbed. With salts of a polybasic acid (carbonate, sulphate, sulphide, oxalate, tartrate, citrate, phosphate, or arsenate), interchange occurs between adsorbed chromic and polybasic acids.

Sulphuric acid, adsorbed by aluminium hydroxide, is completely displaced by polybasic, but not by monobasic acids. Phosphoric acid, similarly adsorbed, is not displaced by carbonic or chromic acid. These two acids are mutually displaceable from adsorption on aluminium hydroxide, that acid being displaced which is at the smaller concentration. This (equilibrium) effect is probably obtainable with any two acids of similar basicity.

When arsenious sulphide is precipitated by means of hydrogen sulphide in presence of a barium salt, it contains adsorbed barium. When the precipitate is washed with a solution of sodium or potassium chloride, no displacement of barium occurs, whilst with solutions of aluminium, ferric, or chromic chloride, interchange of barium and tervalent metal takes place. E. E. T.

Isotherms of Adsorption of Salts by Manganese Dioxide. MAX GELOSO (*Compt. rend.*, 1923, **176**, 1884—1887; cf. A., 1922, ii, 589).—When ammonium persulphate is added to a solution of manganese sulphate containing copper or nickel salts, the resulting precipitate of manganese dioxide adsorbs these metals. Freshly precipitated manganese dioxide also adsorbs iron from solution. If γ=the millimolecular concentration of adsorbed material per milligram-molecule of total solid phase, and C=the concentration in milligram-molecules of salt remaining in solution, then $\gamma=KC^m$, where m is less than unity; m is independent of the nature of the adsorbed substance and of the adsorbent. K varies with these, being a specific coefficient of the adsorbed substance.

E. E. T.

A New Explanation of Diffusion. III. Influence of Gravity on Diffusion. ALEXANDR SOMMER-BATĚK (*Chem. Listy*, 1923, **17**, 79—81).—Solutions of $N/10$-sulphuric acid are placed in one limb of a Y-tube the other limb of which contains water, the liquids

being separated by mercury contained in the lower limb. The mercury is then gradually withdrawn, so that the liquids are free to diffuse into each other. After the lapse of different periods of time, the liquids are again separated, and layers of the solutions withdrawn at regular intervals in the limbs, by means of exits provided for the purpose, and the concentration of the acid is measured. Similar measurements are made for solutions of barium chloride. R. T.

A New Explanation of Diffusion. IV. ALEXANDR SOMMER-BATĚK (*Chem. Listy*, 1923, **17**, 115—118).—The influence of the surface on contact on the diffusion of liquids is measured by allowing water and $N/10$-sulphuric acid contained in the limbs of U-tubes of different diameters to interdiffuse at constant temperature for given periods of time. Layers of solution at different heights from the bottom of the U-tube are then siphoned off, and their concentration and density measured. The results obtained show that the rate of diffusion is proportional to the diameter of the tube. Certain irregularities observed in the fall of concentration of layers of solution in the sulphuric acid limb are explained as being due to the diffusion of water proceeding in waves, which are reflected from the meniscus and may in time produce points of interference or amplification in the column, where the concentration is considerably different from that of the layers immediately above and below. R. T.

Dialysis of Small Volumes of Liquid. The Lily-pad Dialyser. R. W. WOOD (*J. Physical Chem.*, 1923, 27, 565—566).—A method is described whereby quantities of solutions as small as a single drop of liquid may be dialysed. The dialyser is prepared as follows. A small circular plate of glass is fastened horizontally to a turn-table which is capable of rapid rotation, a few drops of collodion, considerably thinned by ether, are placed in the middle of the plate, and the plate is set in slow rotation. A small camel-hair brush is brought into contact with the edge of the collodion pool, and the brush moved slowly away from the centre, the velocity of rotation being immediately increased, and as soon as the collodion is drawn into a perfect disk the brush is lifted. If properly carried out, the whole operation should be complete in a few seconds, and a very thin disk of collodion with a thick rim produced. After drying the film for a few moments, a few drops of water are placed on the plate and brought in contact with the edge of the disk which separates the membrane from the plate. The plate is then lowered at an angle of 45° into a bowl of water, when the membrane floats off with a perfectly dry upper surface. The solution to be dialysed is added drop by drop to form a globule in the centre of the membrane. A disk 4 cm. in diam. will support 2 c.c. of liquid. If the liquid passing through the dialyser is required, the membrane can be floated off in a deep watch glass and most of the water afterwards pipetted away. If the collodion is diluted with ether as above, the dialysis is slow,

but if it is diluted with a mixture of ether and alcohol it is much more rapid. J. F. S.

The Origin of Osmotic Effects. IV. Hydronodynamic Change in Aqueous Solutions. HENRY E. ARMSTRONG (*Proc. Roy. Soc.*, 1923, [*A*], **103**, 610—618; and *Compt. rend.*, 1923, **176**, 1892—1894).—The author summarises evidence and arguments previously advanced regarding the nature of the processes involved in the dissolution of "salts" in water, and advocating an electrolytic explanation of chemical change, and a chemical explanation of electrolysis. "Water" is regarded as a complex saturated with the "gas" hydrone, OH_2, which is the sole potentially "active" constituent, and becomes active only under conditions which suffice to determine electrolytic change. Ideally pure water would be inert. Electrolysis and chemical change are inseparable reciprocal effects, and change takes place only in a system of three components, such as is known to constitute a voltaic couple. The vapour pressure of water or of a solution is the measure of *free* hydrone molecules present in the liquid. The diminution of pressure when a substance is dissolved in water is a proof that the molecules of hydrone are concerned in the change and are thereby diminished in proportion. The solution acquires attractive properties, due to the presence of solute. The internal activity is increased whilst external activity is diminished. Non-electrolytes all have unit effect per molecular proportion; potential electrolytes have at least twice this effect in sufficiently dilute solutions. The effect produced may be ascribed to the interaction of molecules of the solute and of hydrone. From non-electrolytes, under the influence of conducting impurity, a simple hydrol, H·M·OH, is formed, only a single molecule of hydrone being "distributed" on the molecule of the solute, whatever its magnitude. In the case of potential electrolytes, a reciprocal interchange of the radicles of the salt and of hydrone is postulated. The solute is hydrolated and itself distributed on hydrone, the salt $\overset{+}{R}\overset{-}{X}$ thus giving rise initially to the reciprocal systems $RX{<}^{H}_{OH}$ and $H_2O{<}^{R}_{X}$. As the concentration is reduced, the complex $RX{<}^{H}_{OH}$ is, under the influence of hydrone, increasingly converted into hydronol, $H_2O{<}^{H}_{OH}$. Ultimately the solution contains the solute only as $H_2O{<}^{R}_{X}$, together with an equal number of molecules of hydronol. The solute then has maximum (bimolecular) effect. The "distributed" reciprocal complexes, including hydronol, are the electro-chemical agents in a solution. The negative radicle in such complexes has greater residual affinity than it has in the original simple molecules; it is specially attractive of hydrone. Each complex attracts a single hydrone molecule, the molecules thus brought into the solution serving to restore the hydrone equilibrium.

The osmotic pressure of an aqueous solution is the hydraulic pressure exercised by the extra molecules of hydrone attracted into it by the distributed complexes, one by each complex, acting as though they were present in the gaseous state. Osmotic pressure is therefore regarded as *hydronodynamic* in origin, the term expressing the general electrochemical and osmotic activity of water.

J. S. G. T.

Investigation of Ferric Hydroxide Sol. I. A Case of Negative Osmosis. JOHS. LINDEMANN (*Kolloid Z.*, 1923, **32**, 376—383).—The osmosis of ferric hydroxide hydrosol has been investigated. It is shown that with increasing dilution there is a decreasing relationship between the osmotic pressure and the concentration. This is explained by the assumption that the rate of rise of the liquid column is the resultant of the rate at which the liquid passes in and out of the osmotic cell. The velocity outward is increased by the addition of ferric chloride to the sol and under special conditions this can exceed the velocity of the solvent inward. This would naturally bring about a decrease in the level of the liquid column and so explain the decreasing relationship stated above. It is shown that the electrolyte content of a sol can be determinative of the osmotic pressure. J. F. S.

Supersaturation. ROGER G. BOUSSU (*Compt. rend.*, 1923, **177**, 119—121; cf. this vol., ii, 144).—The effect, on the speed of crystallisation, of agitation of, and the presence of nuclei in, supersaturated solutions of potassium hydrogen tartrate and calcium sulphate has been studied. Powdered glass, and, to a less extent, powdered gas carbon, initiate and accelerate such crystallisations.

E. E. T.

Aqueous Solutions. ANDRÉ KLING and ARNOLD LASSIEUR (*Compt. rend.*, 1923, **177**, 109—111; cf. Armstrong, this vol., ii, 542).—The authors consider that simple water molecules may possess one of two structures: $H_2{:}O$ or $H{\cdot}OH$. For further details, the original paper should be consulted. E. E. T.

The Solubility Laws. ALBERT COLSON (*Compt. rend.*, 1923, **176**, 1552—1555).—A critical discussion of views which have been put forward by Le Chatelier with respect to the application of the Clapeyron equation to solutions and to the substitution in that equation of dC/dT for dp/dT, where C is the concentration and the osmotic pressure. The author points out that, assuming the van't Hoff relation $\rho = L - 2T$, the solubility of sodium chloride would decrease with rise of temperature as ρ, which is zero at 63° Abs., should become negative with increase of T, L being constant. Moreover, the substitution of concentration for osmotic pressure ignores the existence of hydrates in solution. Mathematical reasons are also given. The case in which hydrated crystals dissolve in their own water of crystallisation on rise of temperature is discussed. H. J. E.

The Distribution of the Solvent amongst the Dissolved Substances. ANTOINE DOROSZEWSKI (*Bull. Soc. chim.*, 1923, [iv], **33**, 550—559).—A theoretical paper in which it is shown that the author's theory of the distribution of the solvent amongst the dissolved substances in the ratio of the number of molecules of each substance present, gives a satisfactory quantitative and qualitative explanation of the variations of the specific rotatory power of an optically active substance such as sucrose in presence of a dissolved mineral salt such as sodium chloride, and very close agreement is shown between the observed and calculated values for the specific gravity and specific rotatory power of such mixed solutions. Other properties of mixed solutions, such as the electrical conductivity and refractive index, also find an explanation in terms of the theory. G. F. M.

The Graphic Interpretation of the Law of Doroszewski. W. SWIENTOSLAWSKI (*Bull. Soc. chim.*, 1923, [iv], **33**, 560—561).—A graphic method of expressing Doroszewski's law (preceding abstract) is indicated, which facilitates the comparison of the observed and calculated values for any physical property of a mixed solution. The expression is obtained by marking off along the axis of abscissæ the concentrations n_1/n_1+n_2, and on two vertical lines traced from the points $n_1/n_1+n_2=0$ and $n_1/n_1+n_2=1$ (that is to say, the points where the mixture contains 0% and 100% of the substance *A*) the values Z_A and Z_B representing the values of the physical property corresponding with the two solutions, that is, of a molecule of *A* and *N* mols. of solvent, and a mol. of *B* and *N* mols. of solvent. The straight line joining the two points expresses the change of the physical property in any mixture of the two solutions, the total number of dissolved molecules *N* being supposed invariable. G. F. M.

The Specific Heat of Mixtures of Aqueous Solutions of Sodium Chloride and Sucrose. (MLLE) H. BLASZKOWSKA (*Bull. Soc. chim.*, 1923, [iv], **33**, 562—571).—The densities and specific heats of aqueous solutions of sodium chloride and sucrose, and mixtures of such solutions, of concentrations corresponding with 200, 100, 50, and 25 mols. of water per mol. of dissolved substance, were determined to an accuracy of ±0·06%, and the full results are given in tabular form. A perfect agreement was established between the experimental values and those calculated according to Doroszewski's law, according to which the solvent distributes itself among the dissolved substances proportionally to the number of g.-mols. present. Variations from the law did not exceed ±0·12%. G. F. M.

The Influence of a Third Substance on the Miscibility of Phenol and Water. A. BOUTARIC and (MLLE) Y. NABOT (*Compt. rend.*, 1923, **176**, 1618—1620).—An application to phenol-water mixtures of Timmermans's generalisation (A., 1907, ii, 229) that the

miscibility curve of two liquids A and B in the presence of a third substance C lies wholly outside the curve for the pure liquids, the reciprocal solubility of the two liquids being diminished. It was found that the variation produced by a known concentration of a third substance varies with temperature, increasing with rise of temperature for mixtures rich in phenol, and conversely. For a given temperature, the variation depends solely on the concentration of the third substance with respect to the phenol; in those cases in which the third substance is soluble in water, the variation is not so great. The experimental results obtained are qualitatively but not quantitatively in accordance with those obtained by Nernst (A., 1891, 1148). The substances used in the experiments were phenyl salicylate, azobenzene, anthraquinone, and naphthylamine.
H. J. E.

Form of a Crystal as a Function of Superficial Energy and of its Density. CONSTANTIN HRYNAKOWSKI (*Bull. Soc. chim.*, 1923, [iv], **33**, 548—550).—A theoretical paper in which the relationship between crystal form and the density and superficial energy is mathematically developed from the theory of Gibbs and Curie on the conditions of equilibrium in solutions. G. F. M.

Researches on the Relation between the Surface, Mass, and Volume of certain Crystals. K. HRYNAKOWSKI (*Iszy Zjazd Chemików Polskich*, 1923, 14—15; cf. *ibid.*, 14).—It is shown that before the expression $dk/d\sigma \, . \, \sigma+K=F[\sigma \, . \, M_K-f(M_K/d)]$ can be applied to any crystal, it is necessary to obtain the value, P_r, of the function $f(M_K/d)$. P_r, which is the surface of the given crystal, must have as a minimum value that of a sphere of the same volume, P_K, and the ratio P_r/P_K approaches more closely to unity as the symmetry of the crystal increases. For a number of crystalline substances this ratio ranges from 1·579 for copper sulphate to 1·307 for sucrose. R. T.

Coagulative Power of Series of Electrolytes. AGNES IVANITZKAJA and LIDIE ORLOVA (*Koll. Chem. Beihefte*, 1923, **18**, 1—39).—The coagulative power of series of electrolytes has been investigated in connexion with a large number of hydrosols, including the negative sols of mastic, arsenious sulphide, antimony trisulphide, sulphur, gold, platinum, Berlin-blue, manganese dioxide, ferric oxide, and silver bromide, and the positive hydrosols of ferric oxide, alumina, chromic oxide, and silver bromide. The results show that most series of anions with a constant kation are antivalent toward negative sols, but convalent toward positive sols. On the other hand, series of kations with a constant anion are convalent toward negative sols, but antivalent for positive sols. Some few sols, however, give quite irregular results with the series, so that no relationship can be found with the valency; these are to be regarded as exceptions, since they are few in number and occur chiefly in the metal sols or in non-typical sols such as suspensions. Similar experiments were carried out with a few suspensions, including negatively charged suspensions of carbon in solutions

of various alkali hydroxides and tannin, and positive suspensions of ignited alumina and ferric oxide in hydrochloric acid. In these cases, no fundamental difference was found between suspensions and true sols with respect to their coagulation by series of electrolytes. The influence of the addition of methyl alcohol, acetone, glycerol, sodium protalbinate, dextrin, and gelatin in various concentrations to negative suspensions of carbon in potassium hydroxide, positive suspensions of ferric oxide in hydrochloric acid, and hydrosols of gold, platinum, mastic, and silver bromide, on the coagulation phenomena has been investigated. It is shown that the addition of a non-electrolyte to the dispersion medium of a colloidal system changes both the stability of the sol and the orientation of the electrolyte series. The two changes, particularly in the case of anion series, appear to be closely connected. Temperature has apparently no noticeable influence on the coagulation process. It appears generally that the phenomena of coagulation are not the result of any single factor, such as surface tension or dielectric constant, but of very complicated relationships between all the components of the colloidal system, such as the dispersed phase, the dispersion medium, and the coagulating electrolyte. Hence the coagulation series of the electrolytes for different colloidal systems are very different and characteristic. Only in the case of analogous sols are analogous electrolyte series obtained. This is made very clear in the present work, particularly in the series of ferrous-ions, iodate-ions, organic ions, and hydrogen-ions.

J. F. S.

Influence of the Concentration of Reacting Solutions on the Size of the Crystalline Particles of the Precipitates. P. P. von Weimarn (*Koll. Chem. Beihefte*, 1923, **18**, 44—75).—A theoretical paper in which the author considers the criticisms made, in connexion with the crystallisation theory of colloids (A., 1909, ii, 132), by Freundlich (*Kapillarchemie*, 1922, 631); by Buchner and Kalff (A., 1920, ii, 232), and by Bancroft (1920, ii, 295). The author maintains his position, and shows that the criticism offered, so far as it attacks the fundamental principles of the theory, is based on a misunderstanding of the theory. J. F. S.

Non-, Uni-, and Bi-variant Equilibria. XXIII. F. A. H. Schreinemakers (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, 26, 283—296; cf. this vol., ii, 137).—A continuation of the mathematical treatment of equilibria of n components in $n+1$ phases when the quantity of one of the components is infinitesimally small. More particularly the influence of a new substance on a non-variant equilibrium is considered. J. F. S.

The Distribution of Substances between the Gaseous and Liquid Phases, or between Two Liquid Phases. Wojciech Swientoslawski (*I^szy Zjazd Chemików Polskich*, 1923, 17—19).—A formula is deduced from Raoult's law for the distribution of a substance between two liquid phases, or between a liquid and a gaseous phase, namely, $c_1/c_2 \,.\, 1/v\Sigma n = K$, where c_1 and c_2 are the

concentrations of the substance in the liquid and gaseous phase, respectively, v is its molar volume, Σn the total number of molecules present in 1 c.c. of the liquid phase, and k is a constant, the ratio of the densities of the liquid and gaseous substance. Where two substances are present, $1/v\Sigma n = 1/v_1(n_1+n_2) = z$, where n_1 and n_2 are the number of molecules of each substance contained in 1 c.c. of the liquid phase. The distribution formula then becomes $c_1 z/c_2 = k$. For substances obeying Raoult's law, z can vary from 1 to v_2/v_1, the ratio of the molar volumes of the two substances. In those cases where z is very close to 1, which may occur when the solutions are very dilute, or when v_1 is approximately equal to v_2, van't Hoff's law is also obeyed, but as a general rule the latter law and Henry's law can only be regarded as approximations.

R. T.

Equilibrium Conditions of Systems of Three Components. G. G. URAZOV (*J. Russ. Phys. Chem. Soc.*, 1923, **54**, 61—161).—An exhaustive survey is made of graphical methods for the representation of three component systems of all possible types, and under various conditions. The conclusions that can be drawn from such diagrams are pointed out, and the possibility of the prediction on thermodynamical and other grounds of the stability or instability of any system is discussed. R. T.

Influence of Intensive Drying on Internal Conversion. I. A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **26**, 266—269; cf. A., 1922, ii, 358).—The author assumes that every phase contains two different kinds of molecules, an active and an inactive variety, and that these are in equilibrium. Thus in the case of ammonia $NH_3\alpha \rightleftharpoons NH_3\beta$. In intensive drying the equilibrium is shifted to the inactive side, so that the ammonia which remains after the drying contains only inactive molecules. J. F. S.

Kinetic Reactions. I. H. VON EULER and ERIK G. RUDBERG (*Z. Physik*, 1923, **16**, 54—62).—The theory developed by the authors in a previous paper (*Z. anorg. Chem.*, 1923, **127**, 244) is applied to the case of the hydrolysis of ethyl acetate. In the case of a solution of concentration $0{\cdot}05N$, the equilibrium concentration of acetic acid and ethyl alcohol being $0{\cdot}87N$ and that of the hydrochloric acid used as catalyst $0{\cdot}10N$, the respective concentrations of the ions $\left(\begin{matrix}\mathrm{OH}\\ \mathrm{CH_3{\cdot}COEt}\end{matrix}\right)^+$ and $\left(\begin{matrix}\mathrm{O\,H}\\ \mathrm{CH_3{\cdot}C{\cdot}OH}\end{matrix}\right)^+$ inducing the reaction are calculated, and found to be equal to 5×10^{-9}. It is shown that the temperature coefficient of the reaction is dependent on the respective variations with temperature of the coefficient of ionisation of the ester and water, whence it follows that the temperature coefficient of the hydrolysis of ethyl acetate is only slightly greater than that of the ionic dissociation of water. The heat of formation of the salt is therefore small, and it is shown that, as in the case of most salts of inorganic weak bases, the hydrolysis of ethyl acetate increases with increasing temperature. J. S. G. T.

The Mechanism of Reduction. I. H. J. Prins (*Rec. trav. chim.*, 1923, **42**, 473—481).—Essentially an amplification of the previous paper (A., 1922, ii, 488). The following views are put forward: (1) Reduction and oxidation of organic substances are often due to a co-action between the components which can only react through their combined action. (2) Owing to this co-action it is possible to dissolve metals in a medium in which they are normally unattacked, the co-action taking place between the undissociated molecules. (3) Nitrobenzene is strongly adsorbed on to zinc and reacts rapidly with the zinc and acetic acid. Phenylhydroxylamine is less strongly adsorbed; it reacts less rapidly and activates the surface of the zinc. Aniline has no influence on the hydrogen evolution and is not appreciably adsorbed by the zinc. (4) The adsorption may be due to the oxygen atom, which may be oriented towards the zinc. F. A. M.

The Mechanism of Reduction. II. H. J. Prins (*Rec. trav. chim.*, 1923, **42**, 482—495; cf. preceding abstract).—In continuation of the work on co-action and the increased solubility of metals in certain acids in the presence of reducible substances, a detailed examination has been made of the action of acetic acid on zinc in presence of nitrobenzene, phenylhydroxylamine, and aniline.

Nitrobenzene.—In concentrations of about 0·01 to 0·03 mol. solution in 82·4% acetic acid at 78° nitrobenzene does not influence the reaction between pure zinc and acetic acid, but after some time the phenylhydroxylamine formed exerts an accelerating influence on the hydrogen evolution. At 55°, a solution of 0·04 mol. of nitrobenzene in acetic acid has no influence on the hydrogen evolution with commercial zinc. Besides the evolution of hydrogen, a reduction of the nitrobenzene takes place with a velocity ten to twenty times greater than that of the hydrogen evolution, expressed in weight of zinc dissolved, at 55° in 0·0376 mol. solution.

Phenylhydroxylamine.—In a solution of phenylhydroxylamine in acetic acid the velocity of hydrogen evolution is much greater than the normal one, and at the same time the phenylhydroxylamine is rapidly reduced to inactive aniline. The reduction reaction has a velocity about two to three times that of the evolution of hydrogen at 55° in a 0·0376 mol. solution, expressed in weight of zinc dissolved.

Aniline.—When purified by fractional distillation in a vacuum, aniline increases the velocity of the evolution of hydrogen but if the aniline is purified by means of acetone it is found to be without influence. F. A. M.

Measurement of Reaction Velocity and the Temperature Coefficient of Reaction Velocity. F. O. Rice and Martin Kilpatrick, jun. (*J. Amer. Chem. Soc.*, 1923, **45**, 1401—1412).—The authors have made a study of the errors occurring in the measurement of velocity of reaction, and have shown how they may be diminished so that the degree of precision of a single experiment is 0·20%. The reaction selected for this investigation was that between acetone and iodine in dilute aqueous solution catalysed

by hydrochloric acid. The results of this action are summarised thus:

Temp.	0°.	24°.	25°.	27°.	35°.
Velocity constant (k)	0·69944	15·187	17·148	21·609	52·840
Degree of precision %	0·10	0·20	0·070	0·14	0·10

The velocity constant k is the average rate of disappearance of iodine in g.-mols. from a litre of solution containing 1 g.-mol. of acetone, 1 g.-mol. of hydrochloric acid, 0·01 g.-equivalent of iodine, and 0·025 g.-mol. of potassium iodide. The degree of precision is calculated by the formula $\sqrt{(e)^2+(t)^2}$, where e is the mean divergence of k from the mean value, and t is the error in the time readings. Using nitric acid as catalyst, the value $k^{25°}\pm 17·137$, with degree of precision 0·14%, which is the same as that given by hydrochloric acid within the experimental error. With sulphuric acid $k^{25°}=15·543$, degree of precision 0·21%. A method has been developed for determining the temperature coefficient of a reaction with a high degree of precision by a single experiment. For the above reaction, $k^{25}/k^{0}=24·517$ with precision 0·12%, $k^{35}/k^{25}=3·0814$, precision 0·12%. Substituting these values in Arrhenius's equation $2·3026 \log_1 k_1/k_2=Q/R(1/T_1-1/T_2)$, the value of Q is found to be 20695·1, precision 0·038%, and 20431·0, precision 0·11%, respectively. The value of Q therefore diminishes slightly with rise in temperature. It is shown that non-electrolytes have no effect on the temperature coefficient up to concentrations of 30%. J. F. S.

Hydrogenation of Benzene. GREGG DOUGHERTY and HUGH S. TAYLOR (*J. Physical Chem.*, 1923, **27**, 533—557).—A number of experiments on the hydrogenation of benzene under different conditions in the presence of catalysts have been made with the object of gaining an insight by kinetic experiments into the mechanism of the catalytic reduction of benzene to *cyclo*hexane. The results indicate that the reaction does not occur at all according to the stoicheiometric equation, as calculated from gas concentrations, but at rates governed by the distribution of the reacting materials between the catalyst and the gas phase. The trend of the reaction with change of temperature has been studied, and equilibrium values at higher temperatures have been calculated. The results of the latter show that apparent equilibria in the gas phase, as measured in this way, do not necessarily coincide with those which would be expected on the basis of the ordinary equation representing the reaction. The poisoning effect of water vapour, carbon monoxide, and *cyclo*hexane on the reaction has been investigated. It is shown that water vapour in small amounts, up to 2% of the hydrogen volume used in the reaction mixture, has only a slightly depressing effect on the reaction velocity. Carbon monoxide in small amounts, about 2% of the hydrogen volume, has a very marked poisoning effect, particularly at low temperatures of 100° or below. As the reaction temperature is raised, the poisoning is less noticeable. In large quantities, however, round 50% of carbon monoxide the reaction is stopped completely

at 180°. *cyclo*Hexane at low temperatures, 100° or below, has a depressing effect on the reaction velocity. This effect disappears at higher temperatures, in the region of 180°. The experiments show that it is necessary to use great care in making comparative measurements on account of the variability of the nickel catalyst. Different catalysts, although prepared in exactly the same way, may have different activities, and the activity of a given catalyst changes markedly with time and use. The experiments also show that quantitative measurements on a reaction of this kind are difficult, due to the fact that the actual reactant concentrations, on which the velocity of the reaction depends, are those on the catalyst surface, and these concentrations may be independent of, or bear a varying relation to, the reactant concentrations in the gas phase. From experiments at 80° and 90°, it is shown that the temperature coefficient of the reaction is approximately 1·65 for 10° rise. This is evidently the temperature coefficient of a chemical reaction as opposed to that of a diffusion process. J. F. S.

Kinetics of Febrile Reactions: Study of Autocatalysis. A. Quartaroli (*Gazzetta*, 1923, **53**, i, 345—368).—The author discusses the mechanism of reactions which show an initial period of incubation, an intermediate period of induction, and a final period of extinction, and are hence known as febrile reactions. The particular reactions examined are that between nitrates and formic acid (cf. A., 1911, ii, 1079), and those between dilute nitric acid and copper, silver, mercury, antimony, bismuth, tin, iron, cobalt, nickel, zinc, cadmium, and aluminium.

The results show that, when free from nitrous acid, nitric acid does not act in solution as a true oxidising agent, its oxidising properties being no greater than those of a nitrate or a sulphate in solution. Thus, in presence of a considerable proportion of carbamide, the action of nitric acid on tin yields exclusively stannous nitrate, and, similarly, nitric acid does not convert ferrous into ferric salts or mercurous into mercuric salts, even at the boiling point, if the solution contains carbamide, an amino-acid, an amide, etc.

Oxidation represents a necessary condition for the dissolution in acid solutions of metals of solution tension less than that of hydrogen, so that nitric acid, freed from nitrous acid by means of carbamide, will not dissolve even minimum traces of copper, silver, mercury, bismuth, etc., provided that in certain of these cases action of atmospheric oxygen is excluded. With metals having solution tensions which are not very high but exceed that of hydrogen, such as cobalt, nickel, lead, and iron, it is found, as a general rule, that oxidation facilitates the dissolution, although not to a marked extent. On the other hand, with metals of high solution tension, such as cadmium, zinc, and aluminium, oxidation retards dissolution; aluminium is so sensitive to this retarding effect that even the feeble oxidising action of either nitric acid free from nitrous acid or sulphuric acid is detectable.

In these reactions, there is no doubt that the reaction is pro-

ceeding, although with extreme slowness, during the period of incubation, and that it is only when the catalyst generated reaches a certain concentration that the reaction assumes the comparatively enormous velocity of the induction period. The author considers it to be quite arbitrary and liable to lead to error to assume in all cases that a reaction proceeding at a high temperature proceeds also, but with greatly diminished velocity, at a lower temperature. Thus, calculation of the velocity of a reaction by extrapolation from experimental results is not always justified, since weakening of the impulse of a reaction by altering the condition of dilution or by lowering the temperature may render this impulse incapable of overcoming the passive resistance of the reaction. This view is illustrated by the mechanical analogy of the rolling of a ball down a plane inclined at various angles.

When a metal with a low solution tension, that is, one for which oxidation is a condition indispensable to attack, is treated with nitric acid, there is one concentration of the latter below which action never occurs and another higher concentration above which action always proceeds regularly. With intermediate concentrations, action either does or does not take place, in dependence on infinitesimal factors which cannot be defined; in just the same way, it is impossible to calculate the time of fall of a sheet of paper through a certain height in still air.

Reference is made to the marked analogy existing between the course and mechanism of these reactions—the action of negative catalysts, the influence of the resistance of the medium, and the great disproportionality between the rapidity of the reaction and the original concentrations of the reacting substances—and various physiological and pathological phenomena. T. H. P.

The Conditions of Reaction of Hydrogen with Sulphur. II. The Catalytic Effect of Oxygen. III. The Mechanism of the Reaction of Hydrogen with Sulphur and its Catalysis by Oxygen. RONALD GEORGE WREYFORD NORRISH and ERIC KEIGHTLEY RIDEAL (T., 1923, **123**, 1689—1705).

The Behaviour of Activated Sugar Carbon in Contact with Hydrogen Peroxide Solution. JAMES BRIERLEY FIRTH and FRED SHEASBY WATSON (T., 1923, **123**, 1750—1755).

Catalytic Actions at Solid Surfaces. XI. The Action of Alumina and certain other Oxides in Promoting the Activity of Nickel Catalyst. E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1923, [*A*], **103**, 586—597).—The authors have investigated the effect of alumina and certain other oxides on the catalytic activity of a simple nickel catalyst and of a nickel catalyst deposited on a support of kieselguhr or kieselguhr extracted with hot aqua regia. In general, the catalytic activity was determined by ascertaining the degree of hydrogenation effected at 180° by 1 g. of catalyst contained in 150 g. of cotton-seed oil through which a current of hydrogen passed. A mode of preparation of a simple

reduced nickel catalyst which afforded concordant results when the preparation was repeated is detailed. Co-precipitation of the respective oxides of aluminium, iron (ferric), magnesium, or silicon (up to about 2%) with the simple nickel catalyst increased the catalytic activity of the latter, but larger amounts reduced the catalytic activity. Co-precipitation of alumina with nickel oxide on the kieselguhr support likewise increased the catalytic activity of the catalyst, but the action was not the same as in the case of the unsupported nickel. The authors consider that the main, and possibly the only, source of stimulation in activity, in both cases, is the production of an increased surface of catalytic nickel owing to the relatively voluminous admixed oxides separating particles of nickel oxide or nickel which would otherwise coalesce. In the case of acid-extracted kieselguhr, removal of the original metallic constituents causes the nickel oxide to penetrate far into the siliceous structure, with the result that it is less accessible both to reduction and to contact with oil and hydrogen. Deposition of alumina on the guhr fills up these inaccessible parts, so that the superimposed nickel oxide is more favourably placed for contact action. It is considered that any oxide of sufficient bulk or apparent volume, resistant to reduction to the metallic state and not specifically toxic to nickel, will act as a "promoter."

J. S. G. T.

Oxidation Catalyses caused by Salts of Copper and Uranium. J. Aloy and A. Valdiguié (*Bull. Soc. chim.*, 1923, [iv], **33**, 572—576).—Salts of copper, particularly those with weak acids, can act both as oxydases and peroxydases. As examples of oxydase action the production of the blue coloration with solutions of quinol in presence of oxygen, the oxidation of pyrogallol, and of tincture of guaiacum, are cited, whilst the peroxydase action is illustrated by the production of the intense red coloration when salts of copper which do not act directly on guaiacol are added to this substance in presence of hydrogen peroxide, by the action of copper salts under similar conditions on indigo-carmine, or benzidine in alcoholic solution, and by the catalysis of the decomposition of potassium iodide by hydrogen peroxide. Uranium salts act as oxido-reducing catalysts, as instanced by the simultaneous oxidation and reduction of dextrose and methylene-blue respectively which is brought about by uranium salts in sunlight in the absence of oxygen. The latter type of catalysis is largely inhibited by the presence of phenols.

G. F. M.

The Periodic Classification of the Elements. Bohdan Szyszkowski (*I-szy Zjazd Chemików Polskich*, 1923, 54—55).—A connexion is shown to exist between the classification used in analytical chemistry and the periodic classification of the elements. A relation further exists between the mobility of ions and their place in the periodic table. Finally, a relation is established between the periodic classification of elements and the morphological nature of the latter and of their derivatives.

R. T.

Isotopes. A New Relation concerning the Periodic System of the Atomic Species. WILLIAM D. HARKINS (*J. Amer. Chem. Soc.*, 1923, **45**, 1426—1433).—It is shown that the periodic system of the atomic species, developed previously by the author (A., 1917, ii, 303), can be most simply represented as a double network of lines, atomic species existing only at the intersections of the lines. The simplest double network is given if the atomic number is plotted on one axis (X axis) whilst the isotopic number is plotted on the other. In this case, a double network of squares is obtained, with alternate heavy and light lines in both directions. It is found that most of the atomic species, and also the most abundant atomic species, occur where both variables are even numbers, that is, where heavy lines intersect each other. The next most favourable type of intersection is that between light lines, where both variables are odd. A moderate number of species of even atomic number but odd isotopic number (and atomic weight) occur, but in general they are not very abundant. In the diagram these lie on heavy vertical but light horizontal lines. The occurrence of these species is related in a very direct way to that of odd atomic and isotopic number (and atomic weight), since in general when the atomic number is not too high, each species of odd atomic weight but even atomic number lies on the same line of constant isotopic number as, and directly between, two atomic species of odd atomic and isotopic numbers (and odd atomic weight). In the neighbourhood of atomic number fifty, this condition is less exacting, since atomic species of even atomic number but odd isotopic number and atomic weight occur when an atomic species of the same isotopic number is present in either the element of next higher or that of next lower atomic number. In general, species of even atomic weight exist at the intersection of heavy lines, where both atomic and isotopic numbers are even. For atomic numbers higher than twenty-eight, that is, in the region of abundant isotopes, this gives a network of squares, continuous in general within the region of stability, and with from four to seven levels in the vertical or n direction. The general form of the region of stability is that of a hyperbolic band, tangential to the M axis at the origin. The species of odd atomic weight form a pattern of their own, which is on the whole like a single set of steps, or of stairs, ascending towards the right. In certain limited regions, one step lies directly over another, but the number of overlying steps is very many less than for those which represent the species of even atomic weight. Attention is directed to a periodicity of two in the number of nuclear negative electrons, and a somewhat less prominent periodicity of two in the number of protons. In both of these, even numbers give predominance over odd numbers in both number of species and in their abundance. Attention is also directed to a periodicity of two in the relative negativeness (number of negative electrons in the nucleus divided by the number of protons in the nucleus) of the nucleus. It is found that for constant even isotopic number the general difference between adjacent atomic species is one α-particle or

p_4e_2. For odd isotopic number and atomic weight the most common difference is half an α-particle or p_2e, although the difference of a whole α-particle often occurs also. Hypotheses concerning these relations are discussed. The periodic diagram predicts the existence of a considerable number of hitherto undiscovered atomic species (isotopes). Of the nineteen elements of even atomic number for which in each case the most abundant isotope is known, the atomic weight and the isotopic number are both divisible by four in all but three cases. This periodicity is made apparent in the diagram by using specially heavy horizontal lines for isotopic numbers divisible by four. J. F. S.

Separation of Isotopic Ions. JOHN G. PILLEY (*Nature*, 1923, **111**, 848).—A claim for priority on behalf of Lindemann against Kendall and Crittenden (this vol., ii, 282). A. A. E.

The Dimensions of Molecules, Atoms, and Ions and the Methods of Measurement. KARL F. HERZFELD (*Jahrb. Radioaktiv. Elektronik*, 1923, **19**, 259—334).—A critical *résumé* of the literature on this subject, in which the relative accuracy of the different methods of determining molecular dimensions is discussed. The collision area of molecules may be determined with fair accuracy from the movement of slow electrons and from viscosity measurements. The critical data give somewhat more accurate relative values for the space occupied by the molecules if the comparison is made for substances with not too widely different critical values. The absolute values are, however, uncertain, and substances with and without dipoles should be treated separately. Good agreement is obtained between the values from viscosity and critical data. In crystals, the distances between the ions can be derived on the assumption made by Bragg as long as extreme cases are avoided (AgI). The methods based on measurements in liquids have little absolute value except for large colloidal particles. With organic molecules, however, the parallelism between the magnitudes deduced from atomic refraction and other properties is very good. The methods based on Röntgen-rays require an essential increase in the accuracy of the experimental method, and dimensions derived from diamagnetic properties are subject to all the uncertainties of the theories of magnetism. Of those methods giving the distance of the nucleus, it is considered that those from optical measurements and fine structure are the most accurate.

Much smaller values are obtained for molecular dimensions in the gaseous than in the crystalline condition, and this is ascribed to the occurrence of phase relationships between the electronic orbits in the latter case which increase the repulsive forces to such an extent that the ions become practically hard, elastic bodies. The forces exerted by molecules in the gaseous state are much weaker. W. E. G.

The Heterocyclic Theory of Valency and Water of Crystallisation. H. T. F. RHODES (*Anal. Fís. Quím.*, 1923, **21**, 149—161; cf. A., 1921, ii, 255, 681).—An exposition of the author's heterocyclic theory of valency and the constitution of crystal hydrates. G. W. R.

Stability of Co-ordination Compounds. T. MARTIN LOWRY (*Chemistry and Industry*, 1923, **42**, 711—715).—The author distinguishes between two fundamentally distinct types of co-ordination, viz., (1) centric co-ordination, such as occurs, *e.g.*, in ferro- and ferri-cyanides, cobalticyanides, cobaltinitrites, and cobaltammines, in which the principal characteristic consists of a shell of electrons clustered round a metallic atom, and (2) cyclic co-ordination such as occurs, *e.g.*, in compounds containing a chelate group (T., 1920, **117**, 1457), and are characterised by the development or completion of a conjugated ring-system by the insertion of a metallic ion. The stability of centric co-ordination complexes depends mainly on the nature of the central atom of metal and appears to attain a maximum in the case of the tervalent cobaltic ion. The stability of a cyclic co-ordination complex depends on the nature both of the conjugated ring system and of the metallic ion. A maximum of stability is attained in conjugated six-atom rings, the polarities of which are identical with those of aromatic compounds. Conjugated four-atom rings are less stable, and the co-ordinated metal is usually ionisable in solution. In the more stable cyclic systems, a proton can take the place of the metallic ion and yield co-ordinated complexes. J. S. G. T.

Lecture Experiment. Demonstration of Solubilities, or of Indicator Action. R. W. THATCHER (*J. Amer. Chem. Soc.*, 1923, **45**, 1471).—Azolitmin, litmus, or any of the common anthocyan pigments of fruits or vegetables, which when in their acid form are soluble in amyl alcohol, may be used. Fifty c.c. of a neutral aqueous solution of the pigment are placed in a tall, narrow, stoppered cylinder and 4 or 5 drops of a *N*/10-alkali other than ammonia are added. An equal volume of neutral amyl alcohol is added, and the mixture gently shaken and allowed to separate. The pigment in its alkaline form will appear exclusively in the water layer. Eight or 10 drops of *N*/10-acid are now added and the mixture is again shaken and allowed to separate, when the pigment in its acid form will have passed into the amyl alcohol layer. J. F. S.

Inorganic Chemistry.

Determination of the Boiling and Condensation Curves of Mixtures of Hydrobromic Acid and Water under a Pressure of 760 mm. E. CARRIÈRE and CERVEAU (*Compt. rend.*, 1923, **177**, 46—48; cf. Pascal, A., 1917, ii, 569).—Two tables of results are given. The first correlates temperature of boiling with the percentage of hydrogen bromide present in the boiling liquid (temperature range, 22—126—101·25°). The second correlates temperature of distillation with the percentage of hydrogen bromide in the distillate (temperature range, 25—126—100·5°). The results conform to the Gibbs–Konovalov law. E. E. T.

The Electrolytic Dissociation of Hydrogen Tribromide and Tri-iodide. MARJAN HŁASKO (*Iszy Zjazd Chemików Polskich*, 1923, 49).—The conductivity of saturated solutions of bromine and iodine in potassium bromide and iodide solutions is measured, and from these data the electrical conductivity of solutions of hydrogen tribromide and tri-iodide is calculated. From this, it is concluded that the acids in question are highly dissociated in solution, being only a few per cent. weaker than hydrogen bromide and iodide.

R. T.

A Hydrate of Iodine. P. VILLARD (*Compt. rend.*, 1923, **176**, 1516—1518).—A hydrate of iodine may be obtained by placing the element in contact with water in an atmosphere of oxygen or nitrogen and submitting it to a pressure of 150 atmospheres. On local cooling with methyl chloride, the formation and disappearance of crystals may be observed at $+3°$ and temperatures below. For the phenomenon to occur at higher temperatures, the pressure must be increased. Compressed oxygen is a better solvent for iodine than nitrogen (cf. A., 1899, ii, 143), and by using it the crystals may be obtained at $+4°$ and 150 atmospheres, also at $+8°$ under a pressure of 330 atmospheres. By using 350 atmospheres, the formation at 8° becomes quite rapid. The crystals are of a fine reddish-violet colour, and may be easily seen in contrast with the brown, aqueous solution of iodine. The author states that iodine is the least volatile substance which forms such a hydrate, and suggests that other substances, such as paraffin, which are soluble in compressed gases (*loc. cit.*) will behave similarly under still higher pressures.

H. J. E.

A Potassium Chlorate Mixture for Generating Oxygen. HARUKAZE UDAKA (*J. Chem. Ind., Japan*, 1923, **26**, 48—59).—A mixture of potassium chlorate 78·0, ferric oxide 7·0, ferrous carbonate 3·0, iron powder 5·0, silicon dioxide 2·0, magnesium oxide 0·3, magnesium chloride 0·0025, and water 5·0%, compressed by about 1,000 lb. per sq. in., and heated in a bomb, evolves oxygen of 98% purity. Ferrous carbonate may be replaced by nickel or cupric carbonate. K. K.

System Sulphur Trioxide. I. A. SMITS (*Proc. K. Akad Wetensch. Amsterdam*, 1923, **26**, 270—273).—A theoretical discussion of some of Le Blanc and Rütle's results on sulphur trioxide (*Ber. Sächs. Akad. Wiss.*, 1922, **74**, 106). J. F. S.

The Formation of Sulphuric Acid by the Chamber Process. E. BRINER and M. ROSSIGNOL (*Helv. Chim. Acta*, 1923, **6**, 647—655).—To study the influence of various factors on the gas reaction in the chamber process, a special apparatus was designed in which the reaction took place in a series of seven glass tubes, provision being made for the measurement of the acid formed in each. The concentration of the reacting gases was varied by varying the proportion of nitrogen. Increase of concentration increased the reaction in such a manner that the time needed to oxidise a given proportion of the sulphur dioxide varied inversely as the square

of the initial concentration. It follows from this relation that the reaction is of the third order. Increasing the pressure has the same effect as increasing the concentration. Increasing the concentration of nitrogen peroxide has an enormous effect on the reaction velocity. Thus increasing the proportion of nitrogen peroxide from 0·5 to 2·43% increased the reaction velocity about twelve times. The possible application of these results to the industry is discussed. E. H. R.

Composition, Purification, and certain Constants of Ammonia. E. C. McKelvy and C. S. Taylor (*U.S. Bur. Standards, Sci. Paper* 465, 1923, 655—693).—From an examination of fifteen carefully purified samples of ammonia, containing less than one part per million of non-condensing gases and less than 0·003% of water, the mean values of its physical properties were found to be as follows: Density of the solid at $-79°$, 0·817 g. per c.c.; at $-185°$, 0·836 g. per c.c.; freezing point, $-77·7°$; vapour pressure at freezing point, 45·2 mm. [Cf. *J.S.C.I.*, 1923, Aug.]

A. R. P.

Specific Volume of Saturated Ammonia Vapour. C. S. Cragoe, E. C. McKelvy, and G. F. O'Connor (*U.S. Bur. Standards, Sci. Paper* 467, 1923, 707—735).—The specific volume of saturated ammonia vapour between $-50°$ and $+50°$ was measured by the pyknometer method and by measuring the refractive index. Above 0°, the values obtained by both methods agreed well with those calculated from the Clapeyron equation; below 0°, however, the pyknometer results are consistently lower and the optical results higher than the Clapeyron values. The following equation represents the results very closely: $\log_{10}\mu'=300[6·46344/\theta-0·106887+0·0356803\log_{10}\theta]+0·0862366\sqrt{406·1-\theta}+0·002667(406·1-\theta)$ where μ' is the specific volume of saturated ammonia vapour in c.c. per g. and θ is the absolute temperature. A. R. P.

Ammonia and the Carbonates of the Potassium Group. H. Pauly (*Ber.*, 1923, **56**, [*B*], 1454—1455).—If potassium, rubidium, or cæsium carbonate is added to saturation to an aqueous solution of ammonia of any concentration at 20°, the mixture becomes divided into two layers; the upper one is a concentrated solution of ammonia containing only about 1% of the carbonate, whereas the lower one is a saturated solution of the carbonate containing about 1% of ammonia. A similar effect is not produced by sodium carbonate or by a number of freely soluble salts, such as potassium acetate, sodium iodide, or potassium cyanide.

If copper acetate is added to the system potassium, rubidium, or cæsium carbonate–ammonia–water, the copper is retained almost exclusively by the solution of the carbonate. Cellulose dissolved in Schweitzer's reagent can therefore be caused to separate by the addition of potassium carbonate solution; the procedure has the advantage over other methods that the cellulose is precipitated slowly in a viscous, compact form. H. W.

Monochloroamine, NH_2Cl. W. MARCKWALD and M. WILLE (*Ber.*, 1923, 56, [*B*], 1319—1325).—An extension of the work of Raschig (A., 1909, ii, 232), involving the isolation of homogeneous chloroamine.

Well-cooled, approximately *N*-solutions of potassium hypochlorite and ammonia are mixed and the product is distilled under diminished pressure at 30—40°, the distillate being cooled in ice. It contains about 10—12% of chloroamine which suffers decomposition to a considerable extent during the distillation. Even at 0°, the solution soon commences to evolve nitrogen and to separate oily drops of nitrogen chloride. Its instability rapidly increases when it is preserved, decomposition being catalytically accelerated by the liberated acid. The course of the change is represented by the equations: $3NH_2Cl=NH_4Cl+2HCl+N_2$, $NH_2Cl+2HCl=NH_4Cl+Cl_2$, and $NH_2Cl+2Cl_2=NCl_3+2HCl$. Attempts to extract chloroamine from its aqueous solution by means of benzene, chloroform, carbon tetrachloride, or ether had only limited success, the last named solvent being the most suitable.

According to Raschig, the decomposition of chloroamine in alkaline solution proceeds smoothly in accordance with the equation: $3NH_2Cl+3KOH=NH_3+N_2+3KCl+3H_2O$. This appears, however, only to be the case when dilute solutions of alkali are employed. With more concentrated solution the reaction takes place partly in accordance with the scheme: $3NH_2Cl+3KOH \longrightarrow 3NH_3+2KCl+KClO_3$.

The isolation of pure chloroamine has been rendered possible by the observations that its aqueous solutions are greatly stabilised by the presence of very small amounts of ammonia. Even under these conditions, however, the concentration of the 10—12% solutions cannot be effected by distillation, since violent explosions invariably occur which are obviously due to the formation of nitrogen chloride. The authors therefore have had recourse to the desiccation of the vapours of the 10—12% solution and condensation of the unabsorbed portions in a U-tube cooled in liquid air. For this purpose, calcium chloride and soda lime are unsuitable, since they influence the slight hydrolysis of chloroamine by water, $NH_2Cl+H_2O \rightleftharpoons NH_3+HClO$, in such a manner that the condensate consists of chlorine monoxide. Better results are obtained with anhydrous potassium carbonate; *chloroamine* is thus obtained as a colourless, crystalline substance, m. p. −66°. It decomposes suddenly at about −50° into nitrogen, chlorine, ammonium chloride, and nitrogen trichloride, and frequently explodes violently, so that its physical properties could not be further investigated. H. W.

Molecular State at Low Temperatures of Dissolved Nitrogen Peroxide. PAUL PASCAL (*Bull. Soc. chim.*, 1923, [iv], 33, 539—548).—As complex additive products of nitrogen peroxide are known to exist, the question of the existence of this substance at low temperatures in a higher state of condensation than N_2O_4 was investigated by cryoscopic methods. The problem was complicated by the formation of mixed crystals of nitrogen peroxide with the

solvents. Solutions in bromoform presented a eutectic corresponding with 23·5% of bromoform and melting at −13·5°. The calculated mol. wt. of the peroxide was 96, corresponding with N_2O_4. In carbon tetrachloride solution, the eutectic temperature was −49° for 8·15% of the dissolved substance. The mol. wt. found was 48, corresponding with NO_2. In bromobenzene, the eutectic mixture melted at −42·5°, and the mol. wt. was 90. In chloroform, a eutectic mixture melting at −68° containing 8·5% of peroxide was formed, the mixed crystals constituting it being almost pure chloroform crystals with mixed crystals containing 46% of peroxide. The mol. wt. of the peroxide was 89. Even at this low temperature, therefore, the peroxide in solution retains the same constitution as in the liquid state. Solutions in chloropicrin and methyl iodide were also studied. The binary system nitrogen peroxide–camphor was also investigated from a concentration of 0—80% of the latter. Two definite compounds, $5N_2O_4,4C_{10}H_{16}O$, m. p. −52°, and $2N_2O_4,3C_{10}H_{16}O$, m. p. −45·5°, were indicated, and three eutectics, the first, m. p. −60°, formed of crystals of the former combination and mixed crystals containing 27% of camphor, the second, m. p. −55·5°, containing 65·5% of camphor, formed of pure crystals of the above two compounds, and the third, m. p. −46·5°, containing 74% of camphor and formed of pure camphor and the compound $2N_2O_4,3C_{10}H_{16}O$.

G. F. M.

The Preparation of Phosphoryl Chloride by the Simultaneous Action of Water and Chlorine on Phosphorus Trichloride. A. A. Vanscheidt and Vadim Michailovitsch Tolstopiatov (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 270—284).—The oxidation of phosphorus trichloride to the oxychloride can be effected by a number of reagents, such as ozone and potassium chlorate. These methods are, however, inconvenient because the reagents and vessels employed must be dry; a very satisfactory yield (about 90%) of phosphoryl chloride can, however, be obtained by passing a stream of chlorine through phosphorus trichloride and adding, drop by drop, an equivalent quantity of water; the end of the reaction is recognised by the formation of phosphorus pentachloride and the yellow coloration of the liquid. The heat of the reaction maintains the liquid at the boiling point until the end; the boiling is then continued artificially for about half an hour. A description is given of the apparatus used. G. A. R. K.

Revision of the Atomic Weight of Boron. Analysis of Boron Trichloride. O. Hönigschmid and L. Birckenbach (*Ber.*, 1923, **56**, [*B*], 1467—1472).—The ratios, $BCl_3 : 3Ag : 3AgCl$, have been determined for three specimens of boron chloride purified by Stock and Kuss (following abstract), the values for the atomic weight of boron thus found being 10·840, 10·818, and 10·825, respectively. The slightly high value of the first series is probably attributable to the presence of a trace of silicon tetrachloride, derived from the action of boron trichloride on the glass with which it had

been in contact during four months. The authors adopt the mean value, B=10·82, which is in close agreement with the figure, 10·83, obtained by Baxter and Scott (A., 1922, ii, 285). H. W.

The Preparation of Pure Boron Chloride and Boron Bromide for the Determination of the Atomic Weight of Boron. ALFRED STOCK and ERNST KUSS (*Ber.*, 1923, **56**, [*B*], 1463—1466).—Boron chloride is agitated during twenty-four hours in sealed glass bulbs with pure mercury and distilled; the process is repeated a second time to ensure removal of free chlorine. The remaining impurities consist of silicon tetrachloride and hydrogen chloride. The product is distilled from a special, all-glass apparatus, and the distillate is collected in three receivers, cooled respectively to −90° to −85°, −120° to −115°, and in liquid air. The first receiver collects boron chloride and silicon tetrachloride, the second retains the purer fraction of boron chloride, and the third serves to condense the hydrogen chloride in addition to a little boron trichloride. The second fraction is distilled repeatedly until the condensates in each receiver have identical tensions. Lastly, the pure boron chloride is submitted to a control distillation and finally collected in small bulbs which are sealed.

Boron bromide is prepared from boron and "atomic weight" bromine, and is purified in the same manner as the chloride. In this instance, the homogeneity of the different fractions is judged by the melting point, −46·0°, since the tension at 0° is too small to permit a sufficiently accurate judgment to be made.

The materials thus prepared have been used by Hönigschmid and Birckenbach in determining the atomic weight of boron (preceding abstract). H. W.

Revision of the Atomic Weight of Iron. Analysis of Ferric Chloride. O. HÖNIGSCHMID, L. BIRCKENBACH, and R. ZEISS (*Ber.*, 1923, **56**, [*B*], 1473—1481).—As mean value of twenty-five individual determinations of the ratios $FeCl_3 : 3Ag : 3AgCl$, the authors have determined the atomic weight of iron to be 55·85. The preparation and the exact analysis of well-defined, sublimed ferric chloride are fully described in the original communication. H. W.

The Appearance of Particles of Colloidal Carbon. HILARY LACHS (*I^szy Zjazd Chemików Polskich*, 1923, 31—32).—Among other particles visible under the ultramicroscope in solutions of colloidal carbon are a number of scintillating particles, which continue to scintillate until the solution dries. These particles must be in the form of plates or prisms. Colloidal carbon solutions exhibit faint double refraction. R. T.

Oxidation of Graphite by means of a Mixture of Silver Dichromate and Sulphuric Acid. L. J. SIMON (*Compt. rend.*, 1923, **177**, 122—124; this vol., ii, 506).—Oxidation of Canadian graphite (99·9—100% purity) by means of this mixture gave a value for carbon percentage (c_1) of 101·3—102·7, apparently owing to the presence of occluded hydrogen, which escapes oxidation.

After heating the graphite, the carbon percentage found was 99·6—100·5.

Sulphuric acid and chromic anhydride gave values for the carbon percentage (c_2) of 72·7—73·25. Oxidation is thus incomplete.

The oxidation of artificial (Niagara), schistous Canadian, Siberian, Madagascan, and laboratory-made graphites, and of plumbago, by the two different methods, gave a roughly constant c_2/c_1 ratio (0·66) for all the samples examined.

Diamond, wood-charcoal, coke, sugar-charcoal, anthracite, and natural coke are only partly oxidised by the silver dichromate method. E. E. T.

Hydrofluosilicic Acid. Maximum Concentration of the Acid at Room Temperatures. C. A. Jacobson (*J. Physical Chem.*, 1923, **27**, 577—580).—Hydrofluosilicic acid is rarely put on the market in concentrations greater than 25%. The author finds that acid of this concentration (25%) can readily be obtained by passing silicon tetrafluoride into water. This solution can be concentrated to 40—45% by distilling in a double distillation flask at the ordinary temperature while a gentle stream of air is passed through the distilling liquid. Further concentration is effected by vacuum distillation at the ordinary temperature. For this purpose, two glass flasks of about 500 c.c. capacity with ground necks are connected by means of ground joints by a glass tube which is fitted with a side tube carrying a stopcock. A quantity (about 300 c.c.) of solution (41·41%) is placed in one flask, *A*, and the other flask, *B*, is placed in a freezing mixture, the whole exhausted (to 8 mm.) and kept at 20—22°, and periodically the concentrations of acid in *A* and *B* are estimated. The results show that the concentration of acid in *B* increases with the concentration in *A*, and that a maximum concentration of 60·92% is obtained in *A*. Acid of this concentration is stable for long periods of time, perhaps indefinitely. J. F. S.

Influence of Neutral Salts on Silica Gels. S. Glixelli (*Compt. rend.*, 1923, **176**, 1714—1716).—An augmentation of the acidity of silica gels under the influence of a neutral salt such as sodium, potassium or calcium chloride, sodium sulphate, etc., was indicated by titrating the gel with 0·01*N*-sodium hydroxide with phenolphthalein as indicator. The acid properties of silica increase, therefore, as do those of carbonic anhydride, in presence of uni- or bi-valent ions of a neutral salt. The effect can be explained by the adsorption of OH-ions by the silica particles, with which corresponds an increase in the negative charge of the colloidal particles.
G. F. M.

Decomposition of Potassium Chlorate. I. Spontaneous Decomposition Temperatures of Mixtures of Potassium Chlorate and Manganese Dioxide. F. E. Brown, J. Austin Burrows, and H. H. McLaughlin (*J. Amer. Chem. Soc.*, 1923, **45**, 1343—1348).—When homogeneous, finely divided mixtures of potassium chlorate and manganese dioxide in various proportions

are rapidly heated, those containing more than one-sixteenth molecular equivalent and less than five molecular equivalents of manganese dioxide to one molecular equivalent of potassium chlorate undergo a spontaneous decomposition, accompanied by a rapid rise of temperature, at a temperature which is characteristic for each mixture. This acceleration is due to the exothermal nature of the decomposition. Pressure of oxygen exerts a marked effect on the decomposition of potassium chlorate. The decomposition temperature for mixtures containing 6 mol.% of manganese dioxide is 375°; 9%, 350°; 11%, 340°; 14%, 330°; 20%, 317°; 33%, 300°; with larger amounts of manganese dioxide up to about 60% the temperature does not fall much more, but above 60% it rises; thus with 84% of manganese dioxide the decomposition temperature is 315°. J. F. S.

Oxidations with Fluorine. I. FR. FICHTER and K. HUMPERT (*Helv. Chim. Acta*, 1923, 6, 640—642).—The formation of potassium persulphate by the action of fluorine on a solution of potassium hydrogen sulphate was observed qualitatively by Brunner (A., 1921, ii, 45). Using the convenient method for preparing fluorine described by Meyer and Sandow (A., 1921, ii, 398), the observation has been confirmed. When the gas is passed into the cold saturated aqueous solution of potassium hydrogen sulphate for ten to twelve hours the persulphate crystallises out; after three recrystallisations from water, it is pure, having the composition $K_2S_2O_8$. Persulphates have previously only been obtained from hydrogen sulphates by electrolysis. E. H. R.

The Influence of the Formation of Hydrates and Double Salts on the Reaction of Double Decomposition of Salts in Aqueous Solution, in the Case of the System Sodium Chlorate–Potassium Carbonate. VL. P. ILJINSKI (*J. Russ. Phys. Chem. Soc.*, 1923, 54, 29—59).—Solubility curves are constructed for the system sodium chlorate–potassium carbonate at 24·2° and at 40°. The solid phases of this system may contain the following salts at 24·2°: $KClO_3$; $NaClO_3$; $Na_2CO_3,7H_2O$; $Na_2CO_3,10H_2O$; $K_2CO_3,2H_2O$; $K_2CO_3,Na_2CO_3,6H_2O$. The solubilities of mixtures of sodium chlorate and carbonate are determined at 24·2° and at 40°, the solid phases at 24·2° being found to contain sodium chlorate, and the hepta- or deca-hydrates of sodium carbonate, and at 40° sodium chlorate and the monohydrate of sodium carbonate. The formation of the heptahydrate at a temperature below its transition point into the decahydrate is explained as being due to the extremely soluble sodium chlorate abstracting so much water from the solution as to cause a shortage of "solvent" water, thus rendering impossible the deposition of the more fully hydrated salt. The solubilities of mixtures of potassium and sodium carbonates are determined at 40°, 24·2°, 10°, and −6°. At 40°, the solid phases may consist of Na_2CO_3,H_2O, $Na_2CO_3,K_2CO_3,6H_2O$, and $K_2CO_3,2H_2O$; at 24·2° and at 10°, they may contain $Na_2CO_3,10H_2O$, $Na_2CO_3,K_2CO_3,6H_2O$, and $K_2CO_3,2H_2O$, whilst at −6°, $Na_2CO_3,10H_2O$, a new double salt hydrate, $Na_2CO_3,K_2CO_3,24H_2O$, and a *hydrate*, $K_2CO_3,3·75H_2O$,

may separate. Similar measurements are made at 40° and at 24·2° for mixtures of sodium and potassium chlorates, which are found to be the only constituents of the solid phases, although evidence is given for the formation of a double salt in solution. This is based on a new criterion for double salt formation, namely, that the solubilities of two salts increase at those concentrations at which the double salt appears, owing to the liberation of water "fixed" to the separate salts, thereby providing more solvent. Thus, the appearance of maxima of density of solutions may serve as an indication of double salt formation. The solubilities of mixtures of potassium chlorate and carbonate at 40° and at 24·2° are determined, the solid phases being $K_2CO_3,2H_2O$, and $KClO_3$. From the results obtained, it is concluded that the most economical proportions of potassium carbonate and sodium chlorate to use for the preparation of potassium chlorate are 71 g. of the former and 67 g. of the latter per 100 g. of water. Using these proportions, potassium chlorate is precipitated quantitatively from the solution, the mother-liquor containing practically pure sodium and potassium carbonates.

The preparation by electrolysis of sodium chlorate from sodium chloride is examined. A steady current is allowed to pass for various intervals of time through a solution of sodium chloride, and the yields of chlorate are measured. It is found that using 6,565 ampere hours a yield of 93% of the total possible from the current is obtained, whilst using 13,195 ampere hours the yield is only 48% of theory. R. T.

Constitution of the Insoluble Alkali Metaphosphates. Paul Pascal (*Compt. rend.*, 1923, **176**, 1712—1714).—The insoluble alkali metaphosphates, as, for example, sodium metaphosphate prepared by the fusion of sodium dihydrogen phosphate at 850°, are not true metaphosphates, but are substances having the properties of colloids, of which certain transformations are irreversible. Sodium metaphosphate dissolves even in a dilute solution of sodium pyrophosphate, giving a viscous liquid, and its apparent molecular weight varies inversely with the dilution. The metaphosphate is precipitated from these solutions by the addition of a few drops of acetic acid as a colloidal mass which, after the removal of the greater part of the water, is as elastic as caoutchouc, and is dispersible in water, giving a liquid of extremely high viscosity which is no longer precipitable by acetic acid. If the insoluble metaphosphate is fused with sodium pyrophosphate, and the calcined product dissolved in water, the above-described phenomena are not reproduced, and the solution presents instead all the analytical characteristics of the true metaphosphates. G. F. M.

Change of Reaction by the Conversion of Secondary and Primary Alkali Phosphates into Pyro- and Meta-phosphates. The Alkalinity of Borax Solutions. Hans Murschhauser (*Biochem. Z.*, 1923, **138**, 6—12).—As a means of determining the relative changes in reaction when primary and secondary sodium phosphates are converted into meta- and pyro-phosphates, the effect

of these salts on the rate of mutarotation of dextrose was investigated. Equivalent quantities of the salts under comparison were dissolved in water, and 100 c.c. of this solution were used to dissolve 5 g. of dextrose in each experiment. $0{\cdot}025N Na_2HPO_4,12H_2O$ gave a mutarotation constant of 24·9 at 20·4°, whilst the $0{\cdot}025N Na_4P_2O_7$, prepared from the disodium phosphate by heating, gave constants of 90·5 and 84·1. $1{\cdot}0N NaH_2PO_4,H_2O$ gave 26·3 and 24·9; after conversion to $NaPO_3$, the value was 10·7. $0{\cdot}1N Na(NH_4)HPO_4,4H_2O$ gave 40·4 and after conversion to $NaPO_3$ in $1{\cdot}0N$ concentration 8·8. It is concluded that conversion of Na_2HPO_4 to $Na_4P_2O_7$ increases the alkalinity, whilst the change of NaH_2PO_4 to $NaPO_3$ lessens the acidity. $M/120 Na_2B_4O_7,10H_2O$ gave, under similar conditions, a mutarotation constant of 27·8, $M/80$ gave 42·4, whilst with $M/12$ solution mutarotation was so rapid that five minutes after solution the $[\alpha]_D$ was +42·5, *i.e.*, below the equilibrium value for aqueous solutions. This low value (which remains constant for some time) is ascribed, not to any change in the sugar, but to a specific action of borax.

J. P.

The Space Lattices of the Lithium Halides. HEINRICH OTT (*Physikal. Z.*, 1923, **24**, 209—212).—Anhydrous lithium chloride, bromide, and iodide have been investigated by the Debye-Sherrer method. On account of their hygroscopicity, these substances were examined in cylinders of waxed paper made air-tight with paraffin wax. Corrections were necessary for the effect of the paper. To avoid the fogging of the plates by the *L*-radiation of iodine, the rod of lithium iodide was surrounded by aluminium foil. The three space lattices were found to be of the sodium chloride type, and from their dimensions, calculated values of the densities were obtained, which agreed closely with the experimental figures. The monohydrate of lithium chloride possesses a space lattice of the cæsium chloride type.

W. E. G.

The Polysulphides of the Alkali Metals. IV. The Polysulphides of Ammonium. JOHN SMEATH THOMAS and RICHARD WILLIAM RIDING (T., 1923, **123**, 1726—1738).

Stability of Bleaching Powder. SHUICHIRO OCHI (*J. Chem. Ind. Japan*, 1923, **26**, 348—385).—The author has studied the effects of water and other common impurities on the stability of bleaching powder, and investigated methods to prevent the decomposition. The decomposition of bleaching powder is greatly accelerated, not only by the uncombined water, but also by the water of crystallisation of the compound OCl·CaCl. At elevated temperature, 45°, the decomposition is quicker and the effect of water is greater than at the ordinary temperature. The stability of bleaching powder is increased by drying at 100° under reduced pressure (50 mm.), without any appreciable loss of available chlorine. Sodium sulphate or soda lime also promotes stability, but is less effective. Calcium sulphate has little effect, and calcium chloride none. When a mixture of bleaching powder and calcium oxide is chlorinated again, a stable substance is produced containing

31—35% of available chlorine. On the decomposition involving loss of available chlorine, ferric oxide and manganese sesquioxide have a great effect, silicon dioxide a little, and aluminium oxide and magnesium oxide none. The decomposition of the completely dried powder may be represented as follows: $Ca(OCl)Cl=CaCl_2+O$; this decomposition is accelerated by admixture with ferric oxide or manganese sesquioxide, but not by aluminium, magnesium, or silicon oxides. Decomposition leading to the formation of chlorate arises from the presence of water; the more water, the more vigorous the decomposition; it may be almost entirely prevented by drying under reduced pressure or by mixing with calcium oxide, sodium sulphate, or soda lime. The evolution of chlorine may be represented as follows: $2CaCl{\cdot}OCl + (x+1)H_2O = CaCl_2 + Ca(OH)_2 + OCl_2 + xH_2O$ and $OCl_2 = O + Cl_2$. The reaction $Ca(OCl)Cl = CaO + Cl_2$ could not be realised. K. K.

Setting of Plaster of Paris. PIERRE JOLIBOIS and CHASSEVENT (*Compt. rend.*, 1923, **177**, 113—116).—From experiments on the solubility, etc., of calcium sulphate (baked at various temperatures) and of the hemi-hydrate, it is concluded that the setting of anhydrous calcium sulphate takes place in three stages: formation of solid hemi-hydrate, dissolution of the latter, and crystallisation of dihydrate. E. E. T.

The Analysis of Bubbles in Glass. RESEARCH STAFF OF THE GENERAL ELECTRIC CO., J. W. RYDE and R. HUDDART, LONDON (*Proc. Physical Soc.*, 1923, **35**, 197—198).—A small piece of glass containing bubbles is contained in one limb of an exhausted U-tube and mercury in the other. The glass is softened by heating, and then disintegrated by plunging the tube into cold water, the mercury being simultaneously thrown on to the glass. Gases liberated from the bubbles are examined spectroscopically in a capillary discharge tube attached to the U-tube. The presence of nitrogen indicates the introduction of air or furnace gases into the glass during ladling, stirring, or pouring. If nitrogen is absent, it is concluded that the bubbles are due to the generation of gas in the glass. J. S. G. T.

The Alkaline-earth Permanganates. M. CRESPI and E. MOLES (*Anal. Fis. Quim.*, 1922, **20**, 693—701; cf. this vol., ii, 161).—A study of the preparation and properties of the permanganates of calcium, strontium, and barium. The thermal behaviour of these permanganates resembles that of the permanganates of the alkali metals. It is shown that hydrates of calcium and strontium permanganates do not exist. G. W. R.

Equilibrium between Lead Iodide and the Iodides of Potassium and Ammonium in Aqueous Solution. (MME) N. DEMASSIEUX (*Compt. rend.*, 1923, **177**, 51—54).—By means of the solubility method, the author shows that, of the various double iodides of lead with potassium and ammonium, only those

($PbI_2,KI,2H_2O$ and $PbI_2,NH_4I,2H_2O$) described by Herty (A., 1896, ii, 474) and by Wells and Johnston (A., 1893, ii, 523) actually exist. E. E. T.

Hydrous Oxides. V. Hydrous Cupric Oxide. HARRY B. WEISER (*J. Physical Chem.*, 1923, **27**, 501—532; cf. A., 1922, ii, 575, 853).—After a discussion of the literature concerning hydrated copper oxides, the author describes a number of experiments on the stability of the granular hydrated oxide, and the action of salts on the precipitated forms of hydrated copper oxide. The results show that no definite hydrates of cupric oxide are known with certainty. Since a hydrated oxide having approximately zero vapour pressure approaches the composition CuO,H_2O, it is usually concluded that a monohydrate exists. This conclusion is shown to be incorrect by the fact that the anhydrous oxide does not take up water at the ordinary temperature when in contact with water, but, on the contrary, the hydrated oxides lose water under these conditions. A crystalline hydrate has been described (A., 1895, ii, 267), but this has been found to consist of pseudo-crystals or granular particles which do not result from its own power of crystallisation. Loss of water takes place more readily from the gelatinous oxide than from the granular oxide, because of the compact structure of the latter. Highly dispersed hydrated cupric oxide is very light blue in colour. The gelatinous oxide in mass has a characteristic clear blue colour which alters slowly at the ordinary temperature, but rapidly at higher temperatures, passing through various shades of blue to green, brown, and finally to black. The continuous change in colour is due to agglomeration of the particles which accompany the spontaneous loss of water. Blue, gelatinous cupric oxide kept at 0° passes spontaneously to a denser and bluer granular product. It is thus possible to obtain any number of hydrated oxides which vary continuously in composition from $CuO+20H_2O$ to $CuO+H_2O$. Hydrated cupric oxide adsorbs ions strongly. If shaken with solutions of neutral salts like sodium chloride or sulphate, hydrolysis takes place and the solution becomes distinctly alkaline owing to stronger adsorption of acid than of base. On account of the strong adsorption of hydrated cupric oxide for certain ions the presence of some salts frequently accelerates slightly the spontaneous loss of adsorbed water. Hydrated cupric oxide may be heated at 100° without darkening in the presence of very small amounts of salts, such as manganous, cobalt, aluminium, chromous, zinc, and copper sulphates, and zinc and cupric chlorides. The stability of hydrated cupric oxide at 100° in the presence of the above-named salts is not due to adsorption of the hydrated oxides of their metals as stated by Bancroft (A., 1914, ii, 250) and by Blucher and Farnau (A., 1914, ii, 841). The evidence against their stabilisation theory is, that hydrated cupric oxides adsorb acids more strongly than bases, that relatively high concentrations of the colloidal hydrated oxides are not effective, and that cupric sulphate is as effective as manganous and chromous sulphates. This latter observation is conclusive, since it is in-

conceivable that a substance should be stabilised by adsorbing some of itself. The absence of darkening cannot be due to the formation of basic cupric salts, since the effective concentration of electrolyte is so low that the ratio of oxide to sulphate in the salts could be no less than $20CuO : SO_4$, which is altogether improbable; and it is not due to the formation of a protecting film of basic salt, since alkali salts which give basic salts under certain conditions hasten rather than retard the blackening. Darkening of the hydrated oxide at 100° does not take place in the presence of suitable concentrations of certain salts owing to a change in the physical character from the highly gelatinous to the granular form of the oxide. Only those salts which hydrolyse appreciably are effective in low concentrations, since the slight solvent action of the hydrogen-ion destroys the gelatinous structure, and the denser granular modification which forms loses water and darkens less readily than the loose voluminous mass. J. F. S.

The System Copper Oxide, Copper Hydroxide, Cuprite, Sodium Hydroxide. ERICH MÜLLER [with MAX KAHLERT, GEORG WIEGAND, ILSE ERNST, and JOHANNES KEIL], (*Z. physikal. Chem.*, 1923, **105**, 73—118).—An investigation of the system copper oxide, copper hydroxide, cuprite, and sodium hydroxide. It is shown that the blue cupric hydroxide is soluble in concentrated solutions of sodium hydroxide to form deep blue solutions, from which, if the hydroxide concentration does not exceed $17N$, dark brown precipitates separate after keeping for some time. The undissolved blue cupric hydroxide also turns brown on keeping. These dark-coloured substances are to be regarded as solid solutions of cupric oxide and cupric hydroxide, the hydroxide content being connected with the concentration of copper in the supernatant liquid. The dehydration of cupric hydroxide takes place through a series of these solid solutions. The solubility of cupric oxide and cupric hydroxide in sodium hydroxide increases with increasing alkali hydroxide concentration, but above a given concentration the solubility again decreases. The solubility of cupric hydroxide is considerably greater than that of cupric oxide. The rising branch of the solubility curve is represented by $C^2_{(NaOH)}/C_{Cu}=K$ and the falling branch by $C^2_{(NaOH)}\cdot C_{Cu}=K'$. The maxima of the solubilities correspond with the transition point of $CuO+H_2O \rightleftharpoons Na_2CuO_2$ and $Cu(OH)_2 \rightleftharpoons K_2CuO_2$, respectively. Hence cupric oxide and hydroxide on treatment with very concentrated alkali hydroxide are converted into cuprite. A sodium cuprite may be crystallised from aqueous alkali hydroxide solution; this substance has a cobalt blue colour and probably the formula Na_2CuO_2. A diagram has been constructed which presents all the possibilities which may occur when cupric oxide or hydroxide is treated with alkali. The view that copper oxide is colloidally dissolved by alkali hydroxide can no longer be maintained. J. F. S.

Complexes in Solutions of Copper and Cobalt Salts. HENRY GEORGE DENHAM and STUART WORTLEY PENNYCUICK (*J. Amer. Chem. Soc.*, 1923, **45**, 1353—1357).—Measurements of the *E.M.F.* of

cells of the type $Co|CoCl_2+xMCl_y||NH_4NO_3(sat)||Hg_2Cl_2,0{\cdot}1NKCl|Hg$ have been made at 25°, where the concentration of the cobalt chloride is kept constant, and where the nature of MCl_y varies as does also the concentration. The salt MCl_y is potassium chloride, magnesium chloride, aluminium chloride, or zinc chloride. The concentration of the cobaltous ion has been calculated in each case. Similar measurements have been made with cells of the type $Cu|CuSO_4+M_x(SO_4)_y||NH_4NO_3||Hg_2Cl_2 0{\cdot}1NKCl|Hg$, where $M_x(SO_4)_y$ is potassium, aluminium, or zinc sulphate. A comparison of the results fails to reveal any striking difference between the behaviour of zinc and aluminium. Were the electro-affinities of zinc and aluminium the only factors in bringing about changes in the colours of solutions of copper and cobaltous salts, it would be expected that the depressions of the ionic concentrations of copper and cobalt would be more noticeable in the case of aluminium than zinc. The above experiments do not confirm this. In all cases, the effect of adding a zinc salt to a solution of a copper or cobalt salt is rather greater than that produced by an equivalent quantity of an aluminium salt, a result probably due to the increased ionisation of the zinc salt. The moving boundary experiments of Donnan and Bassett (T., 1902, **81**, 939), together with the quantitative migration experiments of Denham and Watkins (T., 1919, **115**, 1269; A., 1909, ii, 373), make it probable that the colour changes exhibited by solutions of copper and cobalt salts are intimately associated with complex formation. The results also indicate that still another factor, which may be hydration, also plays a part in the changes. J. F. S.

Association of Mercuric Chloride. F. Bourion and E. Rouyer (*Compt. rend.*, 1923, **177**, 54—56).—From measurements of the boiling point of a number of aqueous solutions of mercuric chloride, it is concluded that the salt is associated to give treble molecules, which are given the extended formula $Hg[HgCl_3]_2$, to bring the compound into line with $K[HgCl_3]$. E. E. T.

Double Decomposition in the Absence of Solvents. II. The Systems of Mercuric Iodide with the Nitrates of Thallium and Alkali Metals. A. G. Bergmann (*J. Russ. Phys. Chem. Soc.*, 1922, **54**, 200—218).—A study of the system HgI_2–$TlNO_3$ shows that these compounds do not interact on melting, and the diagram of state is of a simple type, with a single eutectic point at 192° and a flat portion in the region 33—75 mol.% HgI_2 indicating miscibility of the components. The usual transition points for the modifications of thallium nitrate were observed, namely, 78·5° and 142·5°, m. p. 207°; for mercuric iodide, 129·5°, and m. p. 257—258°, respectively.

The systems of mercuric iodide with the nitrates of ammonium, lithium, sodium, potassium, and rubidium, were not studied in great detail, because it was found that the mutual solubility of the components was very slight; no signs of interaction of the components could be observed. It is suggested that the higher the negative thermal effect of the double decomposition between the

components, the less is their miscibility in the liquid state; thus in the system $AgNO_3$–HgI_2 there is complete miscibility, whilst $LiNO_3$ and HgI_2 are practically immiscible; the thermal effects of their interaction are calculated at −54·48 cal. and −126·4 cal., respectively.

The theoretical views of van Laar (A., 1908, ii, 808), of Eggink (A., 1908, ii, 1043), and of Smits and Bokhorst (A., 1915, ii, 262) are discussed.

G. A. R. K.

Aluminium-Titanium Alloys and the Influence of Titanium on Aluminium. EUGEN VAN ERCKELENS (*Metall und Erz*, 1923, 20, 206—210).—Aluminium–titanium alloys containing up to 30·7% of titanium consist of a mixture of hard, needle-shaped crystals of Al_4Ti in a softer ground mass of aluminium. The compound Al_4Ti melts at 1325° and forms neither eutectic nor solid solution with aluminium. Addition of titanium, in amounts not exceeding 1%, to aluminium removes the combined nitrogen and oxygen and consequently improves the tensile properties; at the same time, the resistance of the metal to attack by salt solutions and by organic acids is appreciably increased. [Cf. *J.S.C.I.*, 1923, 721A.]

A. R. P.

Synthetic Aluminium Silicates and their Relationships to Kaolin. ROBERT SCHWARZ and ALBERT BRENNER (*Ber.*, 1923, 56, [*B*], 1433—1437).—The action of sodium silicate on aluminium chloride in aqueous solution has been investigated, the conditions being so chosen that the mixtures are neutral in reaction. The precipitates are filtered, dried on the water-bath, washed successively with water, alcohol, and ether, and subsequently analysed. The filtrates contain only traces of aluminium in addition to silicic acid and sodium chloride. The influence of concentration is such that the molecular ratio of silica to aluminium hydroxide diminishes with increasing dilution, but is always at least slightly in excess of the proportion 1·5 : 1, thus showing that silica is invariably adsorbed by the primary product, $2Al_2O_3,3SiO_2$. The proportion of silica in the product increases with increasing concentration of sodium silicate, although the latter never enters quantitatively into the reaction; when 6—10 molecular proportions of silicic acid are present, the compound $Al_2O_3,2SiO_2$ is invariably produced which corresponds in composition with natural kaolin, $Al_2O_3,2SiO_2,2H_2O$. A normal silicate, $Al_2(SiO_3)_3$, appears incapable of existence. The primary product of the action is the compound $2Al_2O_3,3SiO_2,xH_2O$, which absorbs silicic acid when left in contact with the solution and tends to pass into the compound $Al_2O_3,2SiO_2$. If the precipitate is heated in contact with the solution, the substance $Al_2O_3,2SiO_2,2H_2O$ (after desiccation at 10°) is obtained. Röntgen spectrographic investigation of the products proves that the primary product, $2Al_2O_3,3SiO_2,6H_2O$, is amorphous, and that from it there is formed in course of time a crystalline substance which is similar or closely related to natural kaolin in structure. The natural product loses its two molecular proportions of water continuously from 360° and becomes anhydrous at 640°. The artificial product loses one molecular pro-

portion up to 260° and the second proportion between 360° and 640°.

It appears, therefore, that in the neutral, aqueous system, Al_2O_3,SiO_2+H_2O, a single compound, $Al_2O_3,2SiO_2,xH_2O$, is capable of formation which is uninfluenced by the presence of an excess of silica or by the period of the reaction; this compound is formed with particular readiness when at least six molecules of silica are present for each molecule of aluminium oxide, as is the case with felspar. H. W.

Permeability of Nickel to Hydrogen. VICTOR LOMBARD (*Compt. rend.*, 1923, **177**, 116—119).—The volume of hydrogen passing in unit time through a given area of nickel (used in disks 0·3—0·4 mm. thick) is an exponential function of the temperature, and is proportional to the square root of the pressure. Temperatures of 370° to 693° and pressures of 11 to 775 mm. were used. E. E. T.

The Constitution of the Higher Oxide of Nickel. OWEN RHYS HOWELL (T., 1923, **123**, 1772—1783).

Chemistry of Hafnium. G. HEVESY (*Chem. News*, 1923, **127**, 33—34).—Zirconium minerals all contain hafnium to the extent of from 1 to 30% of their zirconium content. Typical thorium minerals were found to be free from hafnium. Zirconium and hafnium are best separated by crystallisation of the potassium double fluoride, prepared by melting the zirconium mineral with potassium hydrogen fluoride. The zirconium and hafnium double fluoride are extracted with boiling water which dissolves 25% of potassium zirconifluoride. On cooling the solution, the hafnium salt concentrates in the mother-liquor, the solubility at 20° of the hafnium double fluoride in $N/8$-hydrofluoric acid solution being about 3% and larger than that of the corresponding zirconium compound. Thus by crystallising a solution of 1000 g. of potassium zirconifluoride containing 6% of hydrofluosilicic acid from a 10% hydrofluoric acid solution, and repeating the process four times, the residual 750 g. of the double fluoride contained only 2% of the potassium salt. Alternatively, the crystallisation described may be replaced by crystallisation of the corresponding ammonium compound, or combined with the partial precipitation of zirconium-hafnium compounds with ammonia, or by boiling the solution with sodium thiosulphate. The phosphate of hafnium is appreciably less soluble in concentrated acids than zirconium phosphate, but separation along these lines is tedious. A preliminary determination, employing hafnium containing from 5 to 6% of zirconium, indicates that the atomic weight of hafnium is between 178·4 and 180·2. J. S. G. T.

Germanium. V. Extraction from Germanium Bearing Zinc Oxide. Direct Preparation of Germanium Dioxide Free from Arsenic. Detection of Minute Amounts of Arsenic in Germanium Dioxide. L. M. DENNIS and E. B. JOHNSON (*J. Amer. Chem. Soc.*, 1923, **45**, 1380—1391; cf. A., 1921, ii, 456; 1922, ii, 302).—A new method for the extraction of germanium

from crude zinc oxide is described. Like the earlier published methods for the extraction of germanium from this material, this new method is based on the volatility of germanium tetrachloride, but it is superior to the earlier methods in that it eliminates the necessity for the use of hydrogen sulphide and concentrates germanium by successive distillations with the aid of a column still of new design. By this process, 99% of the germanium in the crude material is recovered, and of this 83% is obtained directly as germanium dioxide, the remaining 16% is recovered indirectly by the return of residual materials to subsequent extractions. The germanium dioxide produced by this method is of exceptional purity. Spectroscopic examination of the material indicated that it contained less than 0·001% of iron and less than 0·0005% of arsenic. J. F. S.

Germanium Oxide. E. L. NICHOLS (*Proc. Nat. Acad. Sci.*, 1923, 9, 248—251).—The intensity of the visible radiation from germanium oxide at temperatures between 837° and 1370° in the spectral regions λλ 0·65 μ, 0·52 μ, and 0·45 μ, and the departure of the radiation from that characterising a black body have been investigated, together with the production of luminescence in the substance by flame excitation. The melting point of germanium oxide, correct to within a few degrees, is 1400°. J. S. G. T.

Preparation of Metallic Sulphides by Double Decomposition. Application to Cuprous Sulphide. (MLLE) GERMAINE MARCHAL (*Bull. Soc. chim.*, 1923, [iv], **33**, 597—602).—The displacement of antimony from antimonious sulphide (stibine) by copper always results in the formation of cuprous sulphide, whatever the proportion of copper employed. The reaction, scarcely perceptible at 500°, occurs readily at 600—700°, and at that temperature is complete in about eight hours, the antimony having volatilised and condensed on the cooler portions of the experimental tube, whilst almost pure cuprous sulphide remains. When insufficient copper is used for the complete formation of cuprous sulphide no cupric sulphide is formed, but instead the compound $3Cu_2S,Sb_2S_3$, which is only slowly decomposed at temperatures above 700°, antimony sulphide subliming without decomposition, leaving finally a residue of cuprous sulphide only. A similar reaction occurs between copper and zinc sulphide at temperatures of 950—1000°, and here again cuprous sulphide and metallic zinc are the only products. G. F. M.

Mineralogical Chemistry.

Crystal Structure of Molybdenite. ROSCOE G. DICKINSON and LINUS PAULING (*J. Amer. Chem. Soc.*, 1923, **45**, 1466—1471).—The mineral molybdenite has been investigated by means of spectral and Laue photographs and with the aid of the theory of space

groups, the simplest structure capable of accounting for the *X*-ray data has been derived. This structure, which is of a new type, contains two molecules of molybdenum disulphide in a hexagonal unit having $d_{0001}=12{\cdot}30$ Å. and an axial ratio 3·90. The molybdenum atoms are at (1/3, 2/3, 1/4) and (2/3, 1/3, 3/4) and the sulphur atoms at (1/3, 2/3*u*), (2/3, 1/3*u*), (1/3, 2/3, 1/2−*u*) and (2/3, 1/3, 1/2 +*u*) where *u* is $0{\cdot}621\pm0{\cdot}004$. In the structure found, each sulphur atom is equidistant from three molybdenum atoms, and each molybdenum atom is surrounded by six equidistant sulphur atoms at the corners of a small triangular prism the altitude of which is $3{\cdot}17\pm0{\cdot}10$ Å. and the edge of which is $3{\cdot}15\pm0{\cdot}02$ Å. The distance from the molybdenum atom to the nearest sulphur atoms is $2{\cdot}41\pm 0{\cdot}06$ Å. The excellent basal cleavage of molybdenite is undoubtedly connected with the relatively great distance between the sulphur atoms. J. F. S.

Cornish Torbernite. WILLY STEINKUHLER (*Bull. Soc. chim. Belg.*, 1923, **32**, 253—255).—A specimen of torbernite from Tincroft consisted of large spangles embedded in quartz. The crystals were quadratic tablets deep emerald in colour with vitreous lustre: hardness 2; d^{17}, 3·68; *n*, 1·594—1·600 (mean). Analysis gave:

H_2O.	P_2O_5.	UO_3.	CuO.	PbO.	Insoluble.	$Fe_2O_3+Al_2O_3$.
14·62	14·40	60·54	8·58	0·11	0·15	0·61

corresponding with the formula $CuO,2UO_3,P_2O_5,8H_2O$.
F. A. M.

Torbernite from Katanga ($CuO,2UO_3,P_2O_5,8H_2O$). WILLY STEINKUHLER (*Bull. Soc. chim. Belg.*, 1923, **32**, 270—271; cf. previous abstract).—Of three specimens of torbernite from Katanga, two only could be purified sufficiently for analysis; these were massive forms; d^{17}, 3·84—3·951; *n*, 1·600—1·618. All the specimens contained lead. Analysis gave:

H_2O.	Insol.	P_2O_5.	PbO.	UO_3.	$Fe_2O_3+Al_2O_3$.	CuO.	Te.	MoO_3.
14·31	0·18	14·42	2·95	60·35	0·88	7·15	0·63	100·87

The water content both here and the Cornish specimen approximates to that of metatorbernite, but the refractive index is intermediate betwen that for torbernite and metatorbernite, whilst the density differs considerably from either of these. The anomalies may be due in part to the lead content, as this element is present in much greater amount than has hitherto been recorded for torbernite. F. A. M.

Natural Gases. IV. F. HENRICH and G. PRELL (*Ber.*, 1923, **56**, [*B*], 1259—1262; cf. A., 1922, ii, 858).—In continuation of previous work, analyses are now recorded of gases evolved from a number of springs the water of which is so constant in composition that they can be influenced but little or not at all by surface waters.
H. W.

Analytical Chemistry.

Sublimation as an Analytical Procedure. J. Hortvet (*J. Assoc. Off. Agric. Chem.*, 1923, **6**, 481—489).—The use of a sublimator is described, whereby numerous organic substances may be estimated and separated from other substances which have different temperatures of sublimation. A. G. P.

A Trap for the Van Slyke Gas Analysis Apparatus. A. T. Shohl (*J. Biol. Chem.*, 1923, **56**, 125—126).—The trap is illustrated in the original. It consists of a tube attached to, and parallel with, the blood pipette, and carries a stop-cock at the top. Any gas or fluid adhering to the tubing of the apparatus after cleaning gradually collects in this trap, and may then be expelled from the apparatus through the stop-cock. E. S.

Method of Estimating the Available Chlorine in Bleaching Powder. Shuichiro Ochi (*J. Chem. Ind., Japan*, 1923, **26**, 185—190).—Among the methods for estimating available chlorine in bleaching powder, Penot's arsenite method only is regarded as trustworthy, Wagner's iodine method being rejected as giving too high results. The author has improved the latter method by using 2—4 c.c. of dilute acetic acid (1 : 1) for 25 c.c. of the testing solution, the chlorate then being without influence. The arsenite method gives results lower than the true value, whilst the iodine method gives somewhat high figures; the difference is chiefly due to the difference of the application of indicator, *i.e.*, outside and inside indicators, the difference between the two methods being 0·2—0·3%. The accuracy of the two methods is of the same order, but when the testing solution or the standard solution is dilute, Wagner's method gives the more accurate result. K. K.

Use of Bromate in Volumetric Analysis. II. Influence of Mercuric Mercury on Bromic Acid Reactions. G. Frederick Smith (*J. Amer. Chem. Soc.*, 1923, **45**, 1417—1422; cf. this vol., ii, 504).—A number of experiments are described illustrating the use of mercuric mercury in causing bromate to be converted entirely into either bromide or free bromine in oxidation reactions. It is shown that mercuric mercury causes bromate to be reduced to bromide entirely, in its action on chlorides, bromides, and iodides. In the presence of mercuric perchlorate the reactions between manganous nitrate, chromic nitrate, nitrous acid, and oxalic acid, respectively with bromic acid yield bromide entirely, whereas in the absence of the mercuric salt the reaction yields free bromine rather than the bromide. This action is not restricted to reactions with bromates; bromides in the presence of sufficient mercuric mercury are not decomposed by potassium permanganate in hot sulphuric acid solution. Further, the oxidation of sodium oxalate solution by potassium iodate in hot sulphuric acid, according to the equation $2KIO_3+5Na_2C_2O_4+6H_2SO_4=I_2+K_2SO_4+5Na_2SO_4+$

$10CO_2+6H_2O$, is entirely prevented by the presence of sufficient mercuric perchlorate. Mercuric perchlorate is prepared by treating mercuric nitrate with a slight excess of 70% perchloric acid and heating to expel the nitric acid. The solution is then boiled until copious fumes of perchloric acid are evolved, allowed to cool, and the pasty mass centrifuged. This salt is preferable to mercuric sulphate or nitrate, since these salts are so readily hydrolysed and, in the case of the sulphate, difficult to obtain free from mercurous sulphate. The preventive action of mercuric mercury is shown to be due to the formation of slightly ionised mercuric halides. J. F. S.

The Distribution of Iodine between Chloroform and Starch Solution, with and without the Addition of Potassium Iodide. J. B. Firth and F. S. Watson (*J. Soc. Chem. Ind.*, 1923, **42**, 308—310T).—The authors find that starch solutions give an immediate blue coloration with solutions of iodine in chloroform of concentrations greater than $N/1000$. The amount of iodine transferred to the starch solution is proportional to the concentration of the starch, and is increased considerably by the presence of a small amount of potassium iodide, up to 0·192 g. per litre. Further additions of potassium iodide increase the amount of iodine transferred, but the increase is not proportional to the potassium iodide added. A starch solution containing 4 g. of starch and 0·384 g. of potassium iodide per litre will detect iodine in a solution of strength $N/20,000$. J. S. G. T.

Estimation of Iodine by Sodium Thiosulphate. F. O. Rice, Martin Kilpatrick, jun., and William Lemkin (*J. Amer. Chem. Soc.*, 1923, **45**, 1361—1365).—In connexion with the estimation of iodine by titration with sodium thiosulphate, the authors have investigated the volatility of iodine solutions and the stability of solutions of sodium thiosulphate. It is shown that iodine solutions have an appreciable vapour pressure of iodine, and that this is reduced in $0·1N$-solutions just as effectively by 2% of potassium iodide as by 4% of potassium iodide. Iodine may be estimated in acid solution if it is added to standard sodium thiosulphate solution in the presence of a buffer solution, which may be either the phosphate or boric acid buffer described by Washburn (A., 1908, ii, 363). Standard thiosulphate solutions should be made up in the purest water obtainable; they may then be standardised and used immediately after preparation. The authors have devised a method of handling and estimating iodine solutions which is as follows. The stock-bottles containing the iodine and thiosulphate solutions are each fitted with a syphon terminating in a stop-cock, the tip of which is drawn out to be 15 cm. long, with internal and external diameters 0·5 and 1·5 mm., respectively. Portions of thiosulphate (10—30 g.) containing a little starch solution were weighed to 0·0005 g. in stoppered conical flasks. Before adding the iodine to the thiosulphate, the tip of the syphon was filled by adding a little iodine to a beaker of water, keeping the tip about 1 cm. below the surface of the water. The tip was then touched against the side of the beaker to remove adhering liquid and placed

in the thiosulphate solution to a depth of 1 cm. and iodine run in until a faint blue colour appeared. The flask was then removed, stoppered, and weighed. The slight excess of iodine added was corrected by means of blank experiments. J. F. S.

Estimation of Iodine in Thyroid Glands and in Thyroid Extracts. R. FABRE and H. PÉNAU (*Bull. Soc. Chim. biol.*, 1923, 5, 341—347).—The iodine in thyroid extract may be estimated by evaporating to dryness with an aqueous-alcoholic solution of potassium hydroxide, and calcining. The residue is dissolved in dilute sodium chloride solution, and filtered from carbonaceous matter. Permanganate is added to change all iodides to iodates, and the excess destroyed by the addition of alcohol. The iodate is then estimated in the usual way by the addition of iodide and acid and titration of the iodine set free. Thyroidin from pigs contained 0·3048% of iodine, from oxen 0·4127%, from sheep 0·399%, and from horses 0·290%. W. O. K.

Standardisation of Solutions used in Iodimetry. STEPHEN POPOFF and F. L. CHAMBERS (*J. Amer. Chem. Soc.*, 1923, **45**, 1358—1360).—A number of experiments are described on the standardisation of solutions of sodium thiosulphate by iodine and by potassium permanganate, respectively. Ordinarily, the two methods do not give identical results, the former being about 0·1% higher than the latter. It is pointed out that the divergence between the two results is probably to be attributed to the fact that the one titration is carried out in acid solution and the other in neutral solution. The authors show that if both determinations are carried out under identical conditions the result is the same in both cases. The method of titration recommended is: *Iodine method.*—The usual procedure is followed except that the iodine solution, before titration, contains 140 c.c. of water, 10 g. of potassium iodide, and 15 c.c. of 1 : 5-sulphuric acid. *Permanganate method.*—To 100 c.c. of 10% potassium iodide solution containing 15 c.c. of 1 : 5-sulphuric acid a quantity of standard potassium permanganate is added sufficient to liberate about the same quantity of iodine as is normally used in the standardisation of sodium thiosulphate by the iodine method. The liberated iodine is then titrated in the usual way with sodium thiosulphate. Both methods have been used to standardise a given solution of thiosulphate; the iodine method gives the normality of the solution as 0·10053, whilst the permanganate method gives 0·10052. J. F. S.

Estimation of Sulphur in Iron. TERUO ASHIDA (*J. Chem. Soc. Japan*, 1923, **44**, 483—491).—Amongst the methods for the estimation of sulphur in iron or steel, the hydrogen sulphide method gives lower values than the gravimetric method, but takes a shorter time. By the following modification, however, accurate results may be obtained: 2—3 g. of the granulated sample are placed in an Erlenmeyer's flask with about 10 g. of amalgamated zinc (prepared from 8 g. of mercuric chloride and 500 g. of granulated zinc), and hydrochloric acid (*d* 1·15—1·2) is gradually added. When

the reaction becomes feeble, the flask is heated and the gas washed out with hydrogen. The evolved hydrogen sulphide, after washing with 60 c.c. of hot water, is led into a wash bottle (A) containing 40 c.c. of water, and then into an absorption bottle containing 10 c.c. of ammoniacal cadmium chloride solution (prepared from 120 g. of cadmium chloride, 1500 c.c. of water, and 600 c.c. of aqueous ammonia) diluted with 50 c.c. of water. The cadmium sulphide produced is filtered, washed, and titrated with $N/50$-iodine and about $N/50$-sodium thiosulphate solutions. Hydrogen sulphide absorbed in A is estimated and the amount added to the previous figure. The result is identical with that obtained by the gravimetric method, whilst the time required is about thirty minutes only. K. K.

Volumetric Estimation of Tellurium by the Dichromate Method. VICTOR LENHER and H. F. WAKEFIELD (*J. Amer. Chem. Soc.*, 1923, **45**, 1423—1425).—It is shown that the potassium dichromate titration can be applied successfully to the volumetric estimation of tellurium. Tellurium dioxide in hydrochloric acid solution is oxidised quantitatively to tellurium trioxide by potassium dichromate. Certain very definite steps in the procedure are essential. The weight of tellurium dioxide should be less than 0·3 g. and the solution should contain 2·0% of free hydrochloric acid. The volume of the solution should be approximately 200 c.c. The titration is carried out as follows. To the acid solution of tellurium dioxide an excess of $0{\cdot}1N$-potassium dichromate solution is added, followed in half an hour by a known excess of standard ferrous sulphate solution, the excess of which is subsequently titrated by dichromate, using ferricyanide as an outside indicator. J. F. S.

Estimation of Amino-nitrogen in Compounds Reacting Slowly with Nitrous Acid. D. WRIGHT WILSON (*J. Biol. Chem.*, 1923, **56**, 183—190).—Using Van Slyke's apparatus, the amount of nitrogen evolved, when various substances, mainly purine and pyrimidine derivatives, react slowly with nitrous acid, has been measured. The estimations were carried out at temperatures of from 21—26°; the times of reaction varied from three minutes to five hours. Guanosine, guanylic acid, guanine, and cytosine gave amounts of nitrogen which corresponded with more than the theoretical one amino-group; the amount from allantoin corresponded with nearly two such groups; adenine and adenine nucleotide gave the theoretical amount for one amino-group; xanthine, hypoxanthine, guanidine, and methylguanidine yielded small amounts of gas; none was produced by uric acid, thymine, uracil, uridine, brucine, betaine, or sarcosine.

In the estimation of amino-nitrogen in urine by Van Slyke's method, one-third of the blank may be due to the presence of creatinine. E. S.

Estimation of Free Amino-nitrogen in Proteins. D. WRIGHT WILSON (*J. Biol. Chem.*, 1923, **56**, 191—201).—A comparison of the methods of Van Slyke and of Sörensen has led to

the conclusion that the latter is more accurate. Van Slyke's method may give high results owing to slow hydrolysis of the proteins, or low results due to precipitation. E. S.

A Characteristic Reaction for Hydroxylamine. W. N. HIRSCHEL and J. A. VERHOEFF (*Chem. Weekblad*, 1923, **20**, 319—320).—An ammoniacal solution of diacetylmonoxime in presence of hydroxylamine condenses to dimethylglyoxime, which in presence of nickel gives the well-known red precipitate. A concentration of 1 mg. per c.c. of hydroxylamine gives the precipitate at once in the cold; for small quantities, it is necessary to boil, cool, and neutralise with acetic acid, and in this way 0·01 mg. can be detected.

Care must be taken in preparing the diacetylmonoxime solution, since this partly hydrolyses with warm water, yielding free hydroxylamine, which forms dimethylglyoxime when the solution is made alkaline. S. I. L.

Detection of Nitrates in Vegetable or Animal Material. TH. SABALITSCHKA and C. SCHMIDT (*Ber. Deut. pharm. Ges.*, 1923, **33**, 181—184).—The conditions are given for the application of the diphenylamine test for nitrates in presence of organic matter, bromide, iodide, chromate and chloride together, etc. [See *J.S.C.I.*, 1923, Aug.] T. H. P.

A New Gravimetric Estimation of Nitric Acid. H. RUPE and F. BECHERER (*Helv. Chim. Acta*, 1923, **6**, 674—676).—Di-(α-naphthylmethyl-)amine, prepared by catalytic reduction with hydrogen of α-naphthonitrile, forms an extraordinarily sparingly soluble nitrate and can be used for the estimation of nitric acid. A hot 10% solution of the base in 50% acetic acid is added to a boiling, very dilute solution of the nitrate, and when the solution is allowed to cool, the di(α-naphthylmethyl)amine nitrate separates in glistening leaflets which can be readily filtered and washed with cold water. The only acids which form readily soluble salts with the new base are sulphuric acid and phosphoric acid; other acid radicles interfere with the determination of nitrate by this method. The solubility of the nitrate per 100 c.c. of water is 0·00004 g. at 24° and 0·0795 g. at 100°; in 100 c.c. of alcohol, 0·0446 g. at 21°. The solubility of the hydrochloride is 0·0972 g. per 100 c.c. of water at 21°. As a qualitative reagent, the new base gives a distinct precipitate with a 1 : 100,000 solution of potassium nitrate. The nitrate of di(β-naphthylmethyl)amine has a higher solubility, 0·026 g. per 100 c.c. of water at 20°. E. H. R.

The Estimation of Nitrates in Soils by the Phenol-Disulphonic Acid Method. C. T. GIMINGHAM and R. H. CARTER (*J. Agric. Sci.*, 1923, **13**, 60—62).—In the estimation of nitrates in soil extract by the phenoldisulphonic acid method, using aluminium hydroxide as a decolorising agent (Emerson, *Soil Sci.*, 1921, **12**, 413) untrustworthy results may be obtained where the extracts are filtered through certain kinds of filter-paper. It is shown that with a standard solution containing sodium nitrate equivalent to four

parts of nitrogen per million the most satisfactory agreement is obtained where a coarse filter-paper is used. It is suggested that retention by filter-paper may affect the accuracy of estimations in other methods. G. W. R.

The Quantitative Separation of Arsenic, Antimony, and Tin. G. LUFF (*Chem. Ztg.*, 1923, **47**, 601—602).—The mixed sulphides obtained in the ordinary course of analysis are dissolved in 5 g. of the purest sodium hydroxide dissolved in a little water, and the solution is treated with hydrogen peroxide until colourless, boiled for one hour, and evaporated to 100 c.c. After cooling, the solution is neutralised with hydrochloric acid, treated with twice its bulk of the same acid, and saturated with hydrogen sulphide whilst keeping the vessel cooled in ice. Next day, the precipitate of arsenic sulphide is collected on a Gooch crucible, washed with 2 : 1 hydrochloric acid, then with warm water and dissolved in ammonia and hydrogen peroxide. The solution is boiled, exactly neutralised with acetic acid, and treated with ammonium nitrate and silver nitrate, and the silver arsenate is collected on a Gooch crucible, dried at 120°, and weighed. The filtrate from the arsenic sulphide is evaporated to 100 c.c. and its acidity adjusted so that it contains 14 c.c. of hydrochloric acid per 100 c.c.; after adding 5 g. of ammonium chloride per 100 c.c., the antimony is precipitated by hydrogen sulphide, the precipitate collected in a Gooch crucible, washed, dried, heated at 270° in carbon dioxide, and weighed. Tin is estimated in the filtrate from the antimony sulphide by any convenient method. A. R. P.

New Volumetric Method of Elementary Analysis. L. HACKSPILL and G. DE HEECKEREN (*Compt. rend.*, 1923, **177**, 59—60). —The substance to be analysed is heated with cupric oxide in an exhausted silica tube. Combustion, to give carbon dioxide, nitrogen, and water, is complete in about three hours. The products formed are readily estimated. Water is removed by cooling to $-80°$, etc., subsequently treating with calcium hydride, and measuring the hydrogen produced. Nitrogen and carbon dioxide are measured in the usual manner. E. E. T.

Two Analytical Figures of Interest with regard to Illuminating Gas: "Combustible Power" and Percentage of Nitrogen. MAURICE NICLOUX (*Bull. Soc. chim.*, 1923, [iv], 33, 823—835).—The "combustible power" of a gas is defined as the number of volumes of air necessary for the complete combustion of 100 volumes of the gas. The author describes a simple method for the determination of this figure, using only small quantities of gas (of the order of 50 c.c.), and quotes figures for the gas supply of Paris and of Strasbourg. Determinations of the percentage of nitrogen in the gas show that this figure is larger at the present time than before the war. H. H.

Estimation of Carbon Monoxide in the Air. MAURICE NICLOUX (*Bull. Soc. chim.*, 1923, [iv], **33**, 818—822).—The air, deprived of oxygen, is passed through ox blood containing alcohol

as a preservative and the volume of air necessary for the production of the absorption bands of carboxy-hæmoglobin noted. It is claimed that by adhering strictly to the method of procedure and always using the same apparatus set up in the same way, accurate and comparable results can be obtained. H. H.

[Micro]-estimation of Sodium. A. BLANCHETIÈRE (*Bull. Soc. chim.*, 1923, **33**, [iv], 807—818).—Sodium can be estimated in small quantities of biological materials (blood, fæçes, etc.) by precipitation as the triple acetate of uranium, magnesium, and sodium,

$$3UO_2(OAc)_2,Mg(OAc)_2,NaOAc,9H_2O.$$

The author has investigated the conditions under which this method is applicable. [Cf. *J.S.C.I.*, 1923, Aug.] H. H.

A Method for the Analysis of Alkali Phosphotungstates. R. MELLET (*Helv. Chim. Acta*, 1923, **6**, 656—661).—A sample is ignited in a platinum crucible to estimate water or, in the case of ammonium salts, water and ammonia. To estimate phosphoric oxide, the residue is fused with a mixture of four to five times its weight of mixed sodium and potassium carbonates and, after dissolution, the phosphorus is precipitated as magnesium ammonium phosphate in the usual way. A second precipitation is advisable, and the result obtained is generally 1 to 1·5% too low.

The best method available for estimating the tungsten is to precipitate the phosphotungstate as insoluble quinoline phosphotungstate, and to estimate the phosphoric oxide in the residue obtained by igniting the quinoline salt, the tungstic oxide being obtained by difference. The quinoline salt is precipitated at 60° with a solution containing 20 g. of quinoline in 50 g. of glacial acetic acid. The precipitate must be well washed with a dilute solution of quinoline acetate, and even then it adsorbs a small quantity of alkali. The quinoline precipitates stable complex acids completely, but when the complex is unstable, part of the phosphoric acid may remain in solution. The ignition of the quinoline phosphotungstate requires care to prevent reduction of the tungstic oxide to the blue oxide; if this is formed, it can sometimes be reoxidised with nitric acid. Some complex salts, however, cannot be ignited without reduction of part of the tungstic acid to metallic tungsten which, during the alkaline fusion, adheres to the bottom of the crucible as a tungsten-platinum alloy. Its amount is given by the gain in weight of the crucible.

The alkali metal can be determined as chloride in the solution obtained after precipitation of the quinoline phosphotungstate. In such cases where the precipitation of the phosphoric acid is incomplete, the alkali metal can only be estimated by difference. Ammonia is estimated by the usual distillation process.

E. H. R.

The Titration of Silver- and Chlorine-ions in Presence of Protective Colloids. W. D. TREADWELL, S. JANETT, and M. BLUMENTHAL (*Helv. Chim. Acta*, 1923, **6**, 513—518).—Silver nitrate can be titrated electrometrically with sodium chloride in presence

of a protective colloid such as gelatin without appreciable loss of sharpness at the end-point. From the titration curve, it is calculated that the solubility of the colloidal silver chloride is about 2×10^{-2} millimols. per litre, which is about twice the solubility of ordinary silver chloride. The colloidal silver chloride particles introduce no error through adsorption of chlorine- or silver-ions, although such errors are observed in the titration of silver with sulphide. The electrometric titration with chloride is applied in the estimation of ionic silver in a number of pharmaceutical preparations containing silver. [Cf. *J.S.C.I.*, 1923, Aug.] E. H. R.

New Gravimetric Method for the Estimation of Zinc. G. Spacu (*Bul. Şoc. Ştiinţe Cluj*, 1923, **1**, 361—364; from *Chem. Zentr.*, 1923, ii, 508).—An excess of ammonium thiocyanate, either solid or in concentrated solution, is added to a neutral solution of a zinc salt. Pyridine is then added with agitation (3 drops to each 0·1 g. of zinc sulphate) until present in excess. The precipitate, which has the composition $Zn(C_5NH_5)_2(CNS)_2$, is collected and washed with an aqueous solution containing 0·3% of ammonium thiocyanate, 0·2% of ammonium sulphate, and 0·2% of pyridine. The precipitate is dried, ignited over a Teclu burner, and weighed as zinc oxide. The results are in good agreement with those obtained electrolytically. G. W. R.

The Estimation of Metallic Sulphides by Ignition in Hydrogen Sulphide. L. Moser and E. Neusser (*Chem. Ztg.*, 1923, **47**, 541—543, 581—582).—Lead sulphide is stable in an atmosphere of hydrogen or of hydrogen sulphide up to 350°. It begins to volatilise in the latter gas at 570°. Lead oxide, sulphate, carbonate, and chloride may all be converted into sulphide quantitatively by ignition in hydrogen sulphide. For the estimation of lead in solution by this process, it is first precipitated from a solution containing a little nitric acid by a current of hydrogen sulphide, and the precipitate is collected on a Gooch crucible, washed, and heated in an air-bath at 300—400° in a current of the gas. Bismuth may be similarly estimated, but the heating is conducted at 270°. Higher temperatures or an atmosphere of hydrogen decompose the compound. Bismuth oxychloride or the precipitated metal, but not the ignited oxide, are quantitatively converted into sulphide by ignition in hydrogen sulphide at 270°. For the estimation of thallium by the process, hydrogen sulphide is passed into the neutral solution of the thallium salt and ammonia is then added to give a distinct alkaline reaction. The precipitate, collected on a Gooch crucible, is ignited in a current of the gas at 300° and weighed as thallous sulphide. To obtain accurate results air must be excluded from the apparatus. Antimony sulphide, precipitated in either the black or red modification, is converted into pure trisulphide at 270° in hydrogen sulphide, whilst tungsten trioxide, especially if freshly precipitated, is converted quantitatively into disulphide at 500° in a current of the same gas. The process is inapplicable to molybdenum, nickel, cobalt, and tin. A. R. P.

The Molybdo-manganimetric Micro-estimation of Copper. GEORGES FONTÈS and LUCIEN THIVOLLE (*Bull. Soc. chim.*, 1923, [iv], **33**, 840—844).—The copper salt may be treated with an alkali to precipitate the hydroxide, which is then dissolved in glycerol and reduced to cuprous oxide with dextrose or formaldehyde. The cuprous oxide is then dissolved in the phosphomolybdic reagent, and the blue oxides of molybdenum so produced are titrated with potassium permanganate. The authors, however, recommend one of the following methods. The copper may be deposited electrolytically on a platinum gauze spiral, the copper dissolved in the phosphomolybdic reagent (warmed gently if necessary), and the titration carried out as before. The second method consists of the precipitation of the copper as a compound with nitroso-β-naphthol, incinerating this to copper oxide which can be reduced in a current of hydrogen, dissolved in the phosphomolybdic reagent as before, and titrated with potassium permanganate. This method is inapplicable in the presence of iron or cobalt. H. H.

Separation of Copper from Selenium. A. ANGELETTI (*Gazzetta*, 1923, **53**, i, 339—341).—When copper and selenium occur together, the former may be precipitated by means of "cupferron," treatment of the filtrate with sulphur dioxide then resulting in precipitation of the selenium. [Cf. *J.S.C.I.*, 1923, 746A.] T. H. P.

Estimation of Copper and its Separation from Cadmium. P. WENGER and N. DÜRST (*Helv. Chim. Acta*, 1923, **6**, 642—647).—When copper is estimated as oxide by precipitation with sodium hydroxide in a porcelain or glass vessel, the silica should always be estimated in the precipitate and a correction applied. The classical cuprous sulphide method is accurate when proper precautions are taken. The method of Girard, which consists in precipitating the copper with sodium hyposulphite and estimating as cuprous sulphide, is very good for copper alone, but not so good in presence of cadmium, as a second precipitation is necessary. The method of Dallimore (A., 1909, ii, 833), which consists in precipitating the copper with hypophosphorous acid as metallic copper and weighing as such, or as oxide, is very accurate and easy to carry out and is always to be recommended for the separation of copper and cadmium. Other methods described in the literature are not recommended. E. H. R.

The Influence of Alkali on the Titration of some Metals with Ferrocyanide. II. W. D. TREADWELL and D. CHEVRET (*Helv. Chim. Acta*, 1923, **6**, 550—559).—See this vol., i, 764.

Estimation of Praseodymium. PAUL H. M.-P. BRINTON and H. ARMIN PAGEL (*J. Amer. Chem. Soc.*, 1923, **45**, 1460—1465).—The effect of heating praseodymium oxalate in air, oxygen, and a vacuum has been investigated. It is shown that heating the oxalate in air gives a residue of constant weight in crucibles of platinum, porcelain, or alundum. This oxide when heated for sixty minutes in hydrogen at 900—950° loses 3·10% of its weight, but on again

heating in air at the same temperature it regains its original weight exactly. Heating the oxide in oxygen causes a slight increase in weight, but this increase is lost on again heating the oxide in air. These results show that the completely reduced oxide is the sesquioxide, Pr_2O_3, whilst the oxide obtained by ignition in the air is Pr_6O_{11}, and not Pr_4O_7 as stated by Welsbach. A volumetric method is described for the estimation of praseodymium. This consists in adding concentrated nitric acid to the sample, 1 c.c. for 0·1 g. of oxide, and heating to effect solution. About 100 c.c. of water are added and the solution is heated at 60—70° and an excess of 0·1*N*-oxalic acid added slowly with constant stirring. The mixture is kept warm for about an hour. The excess of nitric acid is now gradually neutralised with ammonium hydroxide, which is added a few drops at a time at intervals of several minutes until the liquid shows only a faintly acid reaction. The oxalate precipitate is filtered and washed, and the excess of oxalic acid heated at 80° and titrated with potassium permanganate solution after the addition of 10 c.c. of 1 : 1-sulphuric acid. The results for pure praseodymium and for praseodymium with less than 1% of cerium are very satisfactory, but if lanthanum is present they are too high.

J. F. S.

An Improvement in the Colorimetric Estimation of Manganese in Carbon Steels. H. FORESTIER (*Bull. Soc. chim.*, 1923, [iv], **33**, 659—660).—In the estimation of manganese in carbon steels the oxidation method with persulphate can be used successfully colorimetrically with mean errors of only 0·5% on the manganese content if the light employed in the colorimeter is sensibly complementary to that traversing the solutions under examination. In this case, white, diffused light is filtered through a solution of nickel sulphate, and a neutral tint is thus obtained at the eye-piece which is very sensitive to the least variation of luminous intensity. The sources of possible error in the Proctor Smith method—incomplete oxidation of the manganese, and subsequent incomplete reduction—are eliminated by the colorimetric method, as an excess of persulphate can be used to ensure complete oxidation of the manganese to permanganate.

G. F. M.

The Reaction Between Ferric Salts and Alkali Thiocyanates. J. F. DURAND and K. C. BAILEY (*Bull. Soc. chim.*, 1923, [iv], **33**, 654—659).—On shaking ferric chloride with silver thiocyanate in anhydrous ether a red coloration due to ferric thiocyanate, $Fe(CNS)_3$, is produced; but if the ethereal solution is then shaken with water, practically the whole of the coloration is transferred to the water. The violet-red colour which is extracted from the aqueous solution by ether or amyl alcohol in the usual test for iron or thiocyanates where the alkali thiocyanate is in excess, cannot therefore be due to ferric thiocyanate, and it is also shown that if the ferric salt is present in excess the coloration is scarcely transferred to the ethereal layer at all. The addition of a further quantity of alkali thiocyanate, or even of an alkali chloride, determines the solubility

of the coloured substance in ether or amyl alcohol. For this reason, the colorimetric method proposed by Lachs and Friedenthal for the estimation of iron (A., 1911, ii, 542) cannot be used conversely for the estimation of a thiocyanate. The solubility or otherwise of the red coloration in ether or amyl alcohol cannot be regarded as a specific test for the presence or absence of a thiocyanate, as not only is the thiocyanate colour not always soluble in the organic solvents, but, on the other hand, ferric chloride gives with potassium iodide an intense orange-red colour not destroyed by hydrochloric acid, and soluble in amyl alcohol and ether, and with alkaline acetates the colour is likewise soluble in amyl alcohol, although not in ether. G. F. M.

A New Gravimetric Method for the Estimation of Iron and for the Separation of Iron and Manganese. BOGDAN SOLAJA (*Chem. Ztg.*, 1923, **47**, 557).—Iron may be precipitated quantitatively from solutions of ferric salts by addition of so-called infusible white precipitate (NH_2HgCl). The precipitate obtained is dense, filters readily, and is easily washed; on ignition, it leaves a residue of ferric oxide. The method may be used to separate iron from manganese. A. R. P.

Molybdo-manganimetry and its Applications. II. Micro-estimation of Iron. Application to the Estimation of Iron in the Blood. G. FONTÈS and L. THIVOLLE (*Bull. Soc. Chim. biol.*, 1923, **5**, 325—340; cf. this vol. ii, 264).—The principle of the micro-method described is as follows. The iron is reduced to the ferrous state with copper and phosphoric acid, the phosphomolybdate reagent is added, and the blue colour produced is titrated with permanganate. For very small quantities a modification is preferred in which the iron is precipitated with nitroso-β-naphthol. The precipitate is then ignited and reduced to the metallic state in a current of hydrogen. The phosphomolybdate reagent is added and the blue colour titrated. For the estimation of iron in blood, the iron may be precipitated combined with the hæmoglobin by picric acid, and the whole ignited. The iron is then reduced to the metallic state and estimated as above. Alternatively, the organic matter may be destroyed by heating with sulphuric and nitric acids. The mean error by these methods is 2—3%.

W. O. K.

The Molybdo-manganimetric Micro-estimation of Iron. GEORGES FONTÈS and LUCIEN THIVOLLE (*Bull. Soc. chim.*, 1923, [iv], **33**, 844—849; cf. this vol., ii, 581).—Two methods are proposed. First, a ferric salt is reduced to the ferrous state by means of metallic copper in the presence of phosphoric acid, and the copper in the filtrate estimated as previously described (*loc. cit.*). In the second method, the iron is precipitated by means of nitroso-β-naphthol, incinerated to the oxide, reduced to the metallic state, and estimated as in the case of copper. The second method is inapplicable in the presence of copper or cobalt, but small amounts of phosphates do not interfere. H. H.

Dinitrosoresorcinol as a Reagent for the Estimation of Cobalt in the Presence of Nickel and other Metals of the Iron Group. W. R. ORNDORFF and M. L. NICHOLS (*J. Amer. Chem. Soc.*, 1923, **45**, 1439—1444).—When an aqueous solution of dinitrosoresorcinol is added to a solution of cobalt sulphate or chloride, a brownish-red precipitate is formed, which, when dry, has the composition $(C_6H_3O_4N_2)_2Co$. This can be collected in a Gooch crucible and dried to constant weight at 125—130°, when it has the composition given above; at 160—161°, the compound decomposes. The quantitative precipitation is effected as follows. A solution containing about 0·03 g. of cobalt sulphate or chloride is diluted to 50 c.c. and 1 c.c. of hydrochloric acid (*d* 1·17) added. This is warmed and 300 c.c. of a hot aqueous solution of dinitrosoresorcinol (1 g. per litre) are added. A deep red colour but no precipitate is produced. Then, whilst the mixture is stirred, 10 c.c. of a solution of sodium acetate (10 g. of crystallised salt in 100 c.c. of water) are added slowly. A colloidal precipitate is formed; the solution is digested for fifteen minutes over a flame and stirred once after five minutes' heating. A voluminous, brownish-red precipitate is formed which settles after a short time, leaving a clear, reddish-yellow solution. The precipitate is filtered, with gentle suction, in a Gooch crucible, washed with 0·5—1·0% hydrochloric acid until the filtrate is colourless, and dried at 125—130° until of constant weight. This requires about two hours. The results are accurate to about ±1%. In the presence of small quantities of nickel, cobalt is estimated as follows. The cobalt is precipitated as above and allowed to settle; the clear supernatant liquid is then decanted through a weighed Gooch crucible. A very small amount of precipitate collects on the filter, which is washed with 50 c.c. of 0·085*N*-hydrochloric acid. This same acid is then transferred to the precipitate in the beaker and the whole digested for thirty minutes over a low flame. The precipitate is then filtered through the same Gooch crucible and thoroughly washed with 0·5—1·0% hydrochloric acid and the estimation completed as described above. Neither zinc nor manganese forms a precipitate with dinitrosoresorcinol, and experiment shows that in the presence of relatively large quantities of these metals cobalt may be estimated by the method as originally described. Copper is precipitated to some extent by dinitrosoresorcinol, and the precipitate is not dissolved by digesting with hydrochloric acid, so that to estimate cobalt if copper is present the latter element must be removed first. This is accomplished as follows. The solution containing 0·0200 g. of cobalt and 0·06 g. of copper is acidified with sulphuric acid and electrolysed to remove the copper, then neutralised with 1 : 1-ammonium hydroxide and 1 c.c. of hydrochloric acid (*d* 1·17) added. The cobalt is estimated as before. Iron forms a green precipitate with dinitrosoresorcinol which is not dissolved by digesting with hydrochloric acid. To estimate cobalt in the presence of iron, the solution is treated with 5 c.c. of hydrochloric acid (*d* 1·17) and evaporated to 25 c.c., and extracted with ether, which removes most of the iron. The aqueous solution is boiled to remove ether

and treated with dilute ammonia to precipitate the iron, the precipitate is dissolved in acid and reprecipitated, and the combined filtrates are evaporated to 50 c.c., neutralised with dilute hydrochloric acid, 1 c.c. of hydrochloric acid (d 1·17) is added, and the cobalt estimated as before. J. F. S.

New Volumetric Method for the Estimation of Nickel. G. Spacu and R. Ripan (*Bul. Şoc. Ştiinţe Cluj*, 1922, **1**, 325—331; from *Chem. Zentr.*, 1923, ii, 380).—The method depends on the action of potassium or ammonium thiocyanate on nickel salts in the presence of pyridine, whereby the nickel is precipitated as a blue compound, $[Ni(C_5NH_5)_4](CNS)_2$. The excess of thiocyanate may be determined volumetrically by standard silver nitrate solution. A good agreement is shown with electrolytic estimations. G. W. R.

New Gravimetric Method for the Estimation of Nickel and Thiocyanates. G. Spacu (*Bul. Şoc. Ştiinţe Cluj*, 1922, **1**, 314—320; from *Chem. Zentr.*, 1923, ii, 380; cf. preceding abstract).—The method is based on the reaction of nickel salts with ammonium thiocyanate in the presence of pyridine. The complex nickel pyridine thiocyanate, $[Ni(C_5NH_5)_4](CNS)_2$, is washed with 5% aqueous pyridine solution and after ignition weighed as nickel oxide. In the estimation of thiocyanate by the reverse method, a portion of the nickel forms a soluble blue compound, according to the equation $2NH_4CNS + 6C_5NH_5 + 2NiSO_4 + 2H_2O = [Ni(C_5NH_5)_4](CNS)_2$ (precipitate) $+ [Ni(H_2O)_2(C_5NH_5)_2]SO_4$ (soluble compound) $+ (NH_4)_2SO_4$. G. W. R.

The Analytical Value of the "Molybdenum-blue" Reaction. F. Feigl (*Chem. Ztg.*, 1923, **47**, 561).—The solution used for the test for tin described by Hüttig (this vol., ii, 437) has a distinctly oxidising effect on stannous chloride solutions owing to the presence of nitrates. The most sensitive solution for carrying out the test is made by dissolving 1 g. of molybdenum trioxide in a little sodium hydroxide solution, acidifying with hydrochloric acid, and diluting to 200 c.c. The test may be made very sensitive by shaking the solution with a little amyl alcohol, which extracts the blue compound, giving a blue upper layer (cf. Feigl and Neuber, this vol., ii, 508). The blue colour is more stable in the presence of phosphoric or arsenic acid; the actual blue compound appears to a derivative of molybdenum pentahydroxide, possibly the molybdate, in a colloidal form. In support of this, it is shown that the best conditions for the formation of the colour are a low acidity, absence of neutral salts, and a low temperature. A. R. P.

Detection of Small Quantities of Antimony and Bismuth in Biological Liquids. Caille and E. Viel (*Compt. rend.*, 1923, **176**, 1759—1761).—The reaction recently described (this vol., ii, 443) for the detection of alkaloids by the precipitation of their iodoantimonates by means of a potassium iodide–antimonious chloride reagent may be used conversely for the detection of small amounts of antimony. The most satisfactory reagent for this purpose contains 1 g. of antipyrine and 2 g. of potassium iodide in

30 c.c. of water. This reagent is stable and can be kept indefinitely. It gives a golden-yellow precipitate with an antimony solution to which one-fifth of its volume of hydrochloric acid has been added, and as little as 0·025 mg. of antimony can be detected in this way. By using it as a microchemical reaction the sensibility is raised to 1 in 200,000. Under similar conditions, bismuth gives a brick-red precipitate. To apply the reaction for the detection of antimony and bismuth in biological fluids, the samples must be freed from blood and other organic matter by ignition and subsequent solution of the ash in nitric acid, followed by evaporation to dryness. The white ash is then dissolved in hydrochloric acid and the reagent added. G. F. M.

Combustion of Methane in the Presence of Glowing Platinum. J. W. WHITAKER (*Fuel*, 1923, **2**, 201—202).—In estimating methane in mine gases by slowly burning it in contact with a heated platinum spiral, the latter must be raised to a white heat and the gas exposed to the action of it for three to four minutes, otherwise the methane is not completely oxidised. Such incomplete oxidation may be recognised by the value of C/A obtained (C, contraction in volume after combustion; A, amount of subsequent absorption in potassium hydroxide solution), which in place of the theoretical value 2·0 may approach 4·1 or more. In such cases, the gas should be re-exposed to the action of the hot wire, and this treatment repeated until the ratio total C/total A is very nearly 2. The results obtained are usually slightly higher than those of explosion analysis (cf. Hansen and Nielsen, *ibid.*, 115). T. S. W.

Analysis of Gas Mixtures containing Methyl Chloride. RALPH H. MCKEE and STEPHEN P. BURKE (*Ind. Eng. Chem.*, 1923, **15**, 578—579).—In estimating methyl chloride in mixtures containing other components soluble in organic solvents, the acetic acid absorption method (Allison and Meighan, A., 1919, ii, 527) is supplemented by burning the gas mixture, in a measured excess of oxygen, over a strong solution of potassium hydroxide in a combustion pipette. The alkaline solution and washings are filtered to remove, as mercurous oxide, the small amount of mercury which goes into solution during the combustion, the filtrate is neutralised, and the chloride in it estimated. The quantity of methyl chloride found can be checked by the volume of oxygen consumed, if the nature and amount of any other combustible components are known. A discrepancy between the two results indicates the presence of a higher chlorinated compound or of some combustible gas not taken into consideration. The experimental error is less than 0·7%. If ethylene is present, its volume may be estimated approximately by shaking with bromine water under standard conditions, the amount of methyl chloride reacting with the bromine being inappreciable. W. T. K. B.

Examination of Methyl Alcohol. Frequency of the Occurrence of Impurities acting on Potassium Iodide and Iodine, and on Potassium Permanganate. F. RICHARD (*J. Pharm. Chim.*, 1923, [vii], 27, 456—458).—Although commercially pure

methyl alcohol should give no iodoform with potassium iodide, iodine, and sodium hydroxide (absence of acetone, etc.) and should not within fifteen minutes discharge the violet coloration produced by one drop of $N/10$-permanganate, it is difficult to find since the war samples which respond to these tests, and amounts of acetone varying from 4 to 37 g. per litre have been found in various specimens of methyl alcohol examined. G. F. M.

Estimation of Phenols in Blood. NORRIS W. RAKESTRAW (*J. Biol. Chem.*, 1923, **56**, 109—119).—The method is a modification of that of Folin and Denis (A., 1912, ii, 1011; cf. also Pelkan, A., 1922, ii, 399) and is applicable to tungstic acid blood filtrates. Uric acid is precipitated by the addition of zinc chloride and sodium carbonate according to Morris and McLeod's method (A., 1922, ii, 328), and is separated by centrifuging or filtering. Free phenols are then estimated colorimetrically in the filtrate, using a phosphotungstic–phosphomolybdic reagent (phenol reagent) and employing phenol as a standard; conjugated phenols are given by the difference between this result and one obtained after hydrolysis with hydrochloric acid. The precipitate may be used for the estimation of uric acid. E. S.

The Detection of Ethylenic Derivatives in Official Anæsthetic Ether. F. RICHARD (*J. Pharm. Chim.*, 1923, [vii], **27**, 448—455). —The mercurial reagent for the detection of ethylenic compounds in ether, specified by the French codex and consisting of a mixture of a solution of mercuric chloride and a solution of potassium hydrogen carbonate is very unsatisfactory, as it is very unstable and forms an opalescent or cloudy solution even before it can be used, such opalescence being readily mistaken for that produced by ethylenic derivatives. A more satisfactory reagent is that recommended by Denigès prepared by dissolving 50 g. of mercuric oxide in a mixture of 200 c.c. of concentrated sulphuric acid and 1,000 c.c. of water. On shaking this reagent with an equal volume of ether and setting aside for one hour no opalescence should be produced in the aqueous layer. In presence of ethylenic derivatives, a white opalescence passing eventually into a yellow precipitate is obtained. G. F. M.

Investigation of Abnormal Components of Urine: Dextrose. I. G. INGHILLERI (*Boll. Chim. Farm.*, 1923, **62**, 225—227).—Fehling's solution is reduced by creatine, creatinine, uric acid, asparagine, theobromine, caffeine, the urine of patients undergoing "salvarsan" treatment, etc. In none of these cases, however, is reduction observed if the sodium hydroxide of the Fehling's solution is replaced by sodium carbonate and the Rochelle salt by sodium citrate, the reagent being then specific for dextrose. The reagent, which is stable towards light and is stored as a single solution, is prepared by dissolving 185 g. of crystallised sodium carbonate and 160 g. of sodium citrate in about 500 c.c. of water, the solution being heated, cooled, and filtered; 16 g. of crystallised copper sulphate are dissolved in water in the original vessel and the solutions mixed and made up to 1000 c.c.

Two c.c. of the urine is heated to boiling with 6—8 c.c. of the reagent in a test-tube. Excepting with a large proportion of dextrose, when cuprous oxide is precipitated at once, it is necessary to leave the liquid to cool or to rub the sides of the tube with a glass rod. The precipitate or turbidity obtained in presence of dextrose is orange-yellow and readily visible in artificial light. In cases of pronounced uricæmia, the treated urine develops a precipitate or turbidity of the colour of Turnbull's blue if left overnight; thus, the reagent serves also for the detection of uric acid.

T. H. P.

Estimation of Starch Content in the Presence of Interfering Polysaccharides. GEORGE PELHAM WALTON and MAYNE R. COE (*J. Agric. Res.*, 1923, **12**, 995—1006).—The estimation of the starch content of certain materials by a diastase method is rendered impossible by the presence of mucilages, pectins, and similar carbohydrates. In the method proposed, the material is successively extracted on a filter with ethyl ether, 25—35% ethyl alcohol, 95% ethyl alcohol, and finally ether. The material is then gelatinised by boiling with water, and the starch converted by digestion with malt extract. The interfering polysaccharides are precipitated with 60% ethyl alcohol, and after filtration and removal of alcohol from the filtrate by evaporation the starch conversion-products are hydrolysed by dilute hydrochloric acid. The resulting solution is defecated by addition of phosphotungstic acid and the dextrose estimated gravimetrically by copper reduction.

G. W. R.

A New Titrimetric Method for Estimating Formic Acid. L. UTKIN-LJUBOVZOV (*Biochem. Z.*, 1923, **138**, 205—208).—For the estimation of formic acid in distillates from urine, tissues, and culture media, existing methods were found to be unsatisfactory. A titrimetric modification of the gravimetric Skala method was adopted. The mercurous chloride formed by reduction of the mercuric salt by the formic acid, as in the Skala method, is filtered from the acidified solution, washed and oxidised with a known excess of 0·1*N*-iodine, in the presence of 10% potassium iodide. The excess of iodine is estimated by back titration with 0·1-, 0·02-, or 0·01*N*-thiosulphate, according to the amount of formic acid present. Comparison with other methods of estimation gives good results.

J. P.

Estimation of Acetic Anhydride. G. C. SPENCER (*J. Assoc. Off. Agric. Chem.*, 1923, **6**, 493—497).—0·3—0·4 G. of the acetic anhydride is weighed out in a stoppered capsule, which is then transferred to and opened in a 100 c.c. stoppered Erlenmeyer flask containing a cooled mixture of 15 c.c. chloroform and 1 c.c. of aniline. The flask is immediately stoppered, well shaken, and placed in a refrigerator for not less than an hour. The mixture is washed into a 125 c.c. Squibb separating funnel containing 15 c.c. of 10% sulphuric acid and 15 c.c. of water. Ten c.c. of chloroform are used for the transference. The chloroform layer is drawn

off into a second separating funnel containing 15 c.c. of water, shaken, and the chloroform layer drawn off into a flask. A further 10 c.c. of chloroform are added to the liquid in the first separating funnel, shaken, and drawn off into the second funnel, shaken, and drawn off into the flask. The chloroform washings are repeated with 7 c.c. of chloroform. The united chloroform extracts are evaporated nearly to dryness, and the remaining chloroform is removed with an air blast. Ten c.c. of 10% sulphuric are added to the residual crystals and evaporated on a water-bath to about half the volume. Ten c.c. of water are added, and the evaporation is repeated. The acetanilide must be thoroughly hydrolysed, but the acid must not become sufficiently concentrated to decompose the aniline sulphate. The residue is dissolved in 60 c.c. of water, 5 c.c. of concentrated hydrochloric acid are added, and the liquid is titrated with potassium bromide–bromate solution until a slight permanent yellow coloration is obtained. The bromide–bromate can be made with the requisite amounts of the two substances or by dissolving 13·3 c.c. [40 g.] of bromine in a solution of 28 g. of potassium hydroxide which is subsequently boiled. The accuracy of the method is 1%. A. G. P.

Micro-estimation of the Volatile Acidity of Wines. PH. MALVEZIN (*Bull. Soc. chim.*, 1923, [iv], **33**, 849—852).—The wine under examination is distilled with or without the addition of tartaric acid and the distillate is titrated with $N/100$-sodium hydroxide, using phenolphthalein as indicator. The former method gives the total volatile acid, the latter the free volatile acid. H. H.

Estimation of Mucic Acid. E. O. WHITTIER (*J. Amer. Chem. Soc.*, 1923, **45**, 1391—1397).—Mucic acid may be estimated in acid solution by oxidation with an excess of standard potassium permanganate solution at the boiling temperature, followed by a back titration with standard oxalic acid solution and the standard permanganate solution. The same method may be applied to tartaric acid and to racemic acid. A mixture of oxalic and mucic acids may be precipitated quantitatively as calcium salts, the whole filtered, dissolved in sulphuric acid, and the acids estimated in the presence of each other by first titrating the oxalic acid at 50° with standard permanganate and then applying the above method for mucic acid. Tartaric and racemic acids cannot be titrated with any degree of accuracy in the same solution with oxalic acid. Other combinations of organic acids could in all probability be estimated by this method. The fact that the relationships between these dibasic oxy-acids and potassium permanganate are not stoicheiometric under the conditions employed is shown to be due to the production of formic acid, which is further oxidised only to a slight extent under the conditions of the titrations. J. F. S.

The Cryoscopy of Milk. E. M. BAILEY (*J. Assoc. Off. Agric. Chem.*, 1923, **6**, 429—434).—The depression of the freezing point of milk increased regularly with the acidity, the increase approximating closely to 0·003° per 0·01% acidity. Correction for acidity,

outside the range of "normal" milks, should be applied when cyoscopic methods are used to detect added water in milk. A. G. P.

Estimation of Fat in Milk. A. ZEGA and LILLI ZEGA (*Chem. Ztg.*, 1923, **47**, 405).—Five c.c. of milk, 2 c.c. of a weakly ammoniacal solution of ammonium citrate (*d* 1·036—1·040), and 10 c.c. of a mixture of 55 parts of ether and 45 parts of alcohol are successively introduced into a graduated tube sealed at one end and of 20—25 c.c. capacity. The tube is corked and the contents are mixed by agitation. The milk dissolves and on keeping the contents separate into two layers. The volume of the ether-alcohol layer is read off and 1—2 c.c. are removed with a pipette, evaporated, dried, and the fat weighed. The temperature of the liquids should not be below 20° when they are mixed or solution of the milk will not be complete. The graduated tubes are easily cleaned with water and need not be dried before use. H. C. R.

Estimation of Formaldehyde in Paraformaldehyde. P. BORGSTROM and W. G. HORSCH (*J. Amer. Chem. Soc.*, 1923, **45**, 1493—1497).—The iodometric method for the estimation of formaldehyde in paraformaldehyde (Romijn, A., 1897, ii, 166), based on the equation $CH_2O+I_2+3OH^-=H{\cdot}CO_2^-+2I^-+2H_2O$; the peroxide method (Blank and Finkenbeiner, A., 1899, ii, 188), consisting in the oxidation of formaldehyde to formic acid by means of hydrogen peroxide in alkaline solution, and titration of the excess of alkali; the neutral sulphite method (Doby, *Z. angew. Chem.*, 1907, **20**, 353), depending on the reaction $H_2O+CH_2O+Na_2SO_3=CH_2OH{\cdot}SO_3Na+NaOH$; and the oxidation of paraformaldehyde by means of potassium dichromate or potassium permanganate in hot sulphuric acid solution, and estimation of the carbon dioxide evolved (Messinger, A., 1889, 80), all give results in substantial agreement with the figures obtained by the estimation of carbon and hydrogen in the Liebig combustion apparatus, but the fixed alkali method (Smith, A., 1899, ii, 188), based on the reaction $2CH_2O+NaOH=MeOH+H{\cdot}CO_2Na$, gives results about 0·8% low. The last reaction may also occur if, when using the peroxide or iodometric methods, the hydrogen peroxide or iodine is not added sufficiently soon after the alkali. W. S. N.

The Lautenschläger Process for the Estimation of Aldehydes. L. ROSENTHALER and K. SEILER (*Z. anal. Chem.*, 1923, **62**, 385—388).—The estimation of piperonal and of vanillin by Lautenschläger's process (*Arch. Pharm.*, 1918, **256**, 81), involving condensation of the aldehyde and hydrazine to form an aldazine followed by iodometric estimation of the excess of reagent, was found to give results that were much too low. No better results were obtained by effecting the condensation with hydrazine sulphate and determining the liberated acid alkalimetrically; in this case the results were high. A. R. P.

The Error in the Urea-Hypobromite Method. B. M. MARGOSCHES and HEINRICH ROSE (*Biochem. Z.*, 1923, **137**, 542—561).—The cause of the nitrogen deficit in the hypobromite method

for the estimation of urea has been studied; the main error is not due to the solubility of the nitrogen in the hypobromite solution, to oxide formation, or to formation of cyanate, but is due to undecomposed urea. The authors' alkalimetric hypobromite method (this vol., ii, 348) being carried out in warm solution overcomes the difficulty. H. K.

Estimation of Urea alone and in the Presence of Cyanamide by Means of Urease. E. J. Fox and W. J. Geldard (*Ind. Eng. Chem.*, 1923, **15**, 743—745).—An accurate and direct method is given for the estimation of urea, based on its conversion into ammonium carbonate by the action of urease and the subsequent titration of the ammonia. The velocity of the reaction is nearly doubled for each 10° rise of temperature between 10° and 50°, and the activity of the enzyme is destroyed at 80°. Experiments were carried out to determine the safe limits as to time of digestion and concentration of urea and urease. Most salts have a depressing effect on the action of the urease, and those of barium and calcium must be removed. Details are given of the methods of estimating urea alone and in presence of cyanamide and phosphates. The method appears to be of quite general application. H. C. R.

A Microchemical Method of Estimating Hydrocyanic Acid. L. Rosenthaler and K. Seiler (*Z. anal. Chem.*, 1923, **62**, 388—389).—Hydrocyanic acid in small quantities in very dilute solution may be estimated by titration with iodine under the following conditions: the solution is placed in a small flask with a narrow neck and treated with a measured amount of a saturated solution of calcium carbonate, 2 to 3 c.c. of light petroleum are added, and the liquid is titrated with $N/1000$-iodine until a faint permanent brown colour is observed in the petroleum layer which should extend up the neck of the flask. One c.c. of the iodine solution corresponds with 0·0135 mg. of hydrocyanic acid. A. R. P.

The Iodometric Estimation of Small Quantities of Cyanides and Thiocyanates. E. Schulek (*Z. anal. Chem.*, 1923, **62**, 337—342).—The cyanogen group in cyanides and thiocyanates is completely converted into cyanogen bromide by treatment with bromine in slightly acid solution, and the bromide may be estimated iodometrically. The process is carried out as follows: 50 c.c. of a solution containing 0·1 to 40·0 mg. of hydrocyanic acid or 0·3 to 90·0 mg. of thiocyanic acid are treated with 5 c.c. of 20% phosphoric acid and a slight excess of bromine; 30 to 40 drops of a 5% solution of phenol are added, and the mixture is left for fifteen minutes in the dark. 0·5 G. of potassium iodide is dropped into the solution, and, after half an hour in the dark, the liberated iodine is titrated with thiosulphate. Half the molecular weight of either of the acids under examination is the equivalent weight in this process. If it is desired to estimate each acid in the presence of the other, the solution is first distilled with 1 g. of crystallised boric acid, which decomposes cyanides only. The distillate is

collected in weak sodium hydroxide solution and the cyanide content of this is determined as described above, the thiocyanate being estimated similarly in the residue in the distillation flask.
A. R. P.

Detection of Quinine in Presence of Antipyrine and Pyramidone. Domenico Ganassini (*Boll. Chim. Farm.*, 1923, **62**, 321—322).—The red coloration given by chlorine water and ammonia with a mixture of quinine and antipyrine is obtained only when these two substances are present in about equal proportions. The disturbing effect produced by small quantities of antipyrine or pyramidone on the colour reactions of quinine may be obviated by treating the residue of the ethereal extract several times with cold water, which dissolves the antipyrine and pyramidone almost completely and leaves nearly pure quinine. T. H. P.

An Unambiguous Macro- and Micro-chemical Test for Histidine in Protein. Hermann Brunswick (*Z. physiol. Chem.*, 1923, **127**, 268—277).—The diazo-reaction is given both by histidine and by tyrosine, so that if the latter is present, as shown by a positive Millon's reaction, a modification is necessary in testing for histidine. The substance should first be nitrated by warming with dilute nitric acid (20—50%) and then made alkaline with sodium carbonate. Tyrosine no longer gives the diazo-reaction, so that, under these conditions, this test is specific for histidine. It may be applied quantitatively, using a colorimeter, or microchemically, on a microscope slide. W. O. K.

Rapid Method for Estimating Theobromine in Cocoa. Trifon Ugarte (*J. Pharm. Chim.*, 1923, [vii], **27**, 420—423).—The cocoa is heated in a dry Kjeldahl digestion flask until the theobromine is sublimed and the cocoa completely carbonised. The theobromine is extracted with hot water, filtered, and the filtrate evaporated to dryness on the water-bath. The residue is purified by extraction with absolute alcohol, treated with aqueous ammonia, and dissolved in chloroform. The chloroform solution is filtered and evaporated to dryness, the residue extracted three times with 3 c.c. of hot water, filtered, and the filtrate evaporated to dryness on a watch glass, dried at 100—105°, and weighed. The whole estimation takes about two and a half hours. The percentage of theobromine in various samples of commercial cocoa varied from 0·45% to 1·17%. H. C. R.

A New Optical Instrument for the Estimation of Hæmoglobin. H. S. Newcomer (*J. Biol. Chem.*, 1923, **55**, 569—574).—The instrument is a modified Duboscq colorimeter. For the estimation of hæmoglobin, the whole blood is mixed with 1% hydrochloric acid and the solution of acid hæmatin thus obtained compared with a standardised yellow glass (cf. A., 1919, ii, 179) which is incorporated in one of the plungers of the hæmoglobinometer. The instrument is calibrated to read percentage of hæmoglobin. E. S.

General and Physical Chemistry.

Refraction Equivalents of Ions and the Structure of Compound Ions. JARL A. WASASTJERNA (*Soc. Sci. Fennica Com. Phys.-Mat.*, 1923, **1**, No. 37, 1—7).—From previously published data (A., 1922, ii, 1, 2, 491), the author has calculated the ionic refractivities of several uni- and bi-valent ions. The following new values are recorded: $F'=2\cdot20$; $Mg^{\cdot\cdot}=0\cdot44$; $O''=4\cdot06$; $S''=15\cdot0$; $Br'=11\cdot84$; $I'=18\cdot47$; the atomic refractivities of the inert gases have also been calculated and the values Ne=1·01, A=4·23, Kr=6·42, and X=10·56 obtained. It is shown that Cuthbertson's rule, which connects the atomic refractivity with the atomic weight of gaseous elements, is approximately followed by the ions of the alkali and alkaline-earth metals and also by the halogen-ions. But in the latter case the refraction equivalent increases rather more slowly than is required by Cuthertson's rule. The constitution of compound ions, such as NO_3', SO_4'', PO_4''', CO_3'', has been discussed in connexion with the refraction values of these ions. The values calculated for these ions on the basis of the accepted structure of the ions are found to be of much the expected dimensions. It is shown that in the determination of constitution of inorganic ions, the interaction between the central sustaining ion and the electron systems of the surrounding ions is a matter which in all probability cannot be neglected generally. J. F. S.

Radii of Ions. JARL A. WASASTJERNA (*Soc. Sci. Fennica Com. Phys.-Mat.*, 1923, **1**, No. 38, 1—25).—A theoretical paper in which the connexion between ionic radii and refraction equivalents is discussed. The ionic radii of the metals of the alkalis and alkaline-earths, and of the halogens and members of the oxygen group, have been calculated from the refraction equivalents previously obtained (cf. preceding abstract). The values of the ionic radii thus obtained are discussed and compared with similar values found by Bragg (A., 1920, ii, 537), by Fajans and Herzfeld (A., 1920, ii, 174), and by Grimm (A., 1922, ii, 127). J. F. S.

The Optical Constants of certain Liquids for Short Electric Waves. J. D. TEAR (*Physical Rev.*, 1923, **21**, 611—622).—The refractive indices of water, glycerol, methyl alcohol, and ethyl alcohol for short electric waves, λ 4 to 27 mm., have been computed from measured values of absorption and reflection coefficients, some values also being obtained by utilising the phenomenon of interference in thin films. The values of *n* for λ 0·42 cm. and λ 2·7 cm., respectively, are abstracted as follows: Ethyl alcohol, 1·84, 2·27; methyl alcohol, 2·10, 3·3; glycerol, 1·98, 2·53; water, 1·33, 8·45. A. A. E.

Spectrochemical Investigations: [Unsaturated γ-Lactones, Hydroxy-aldehydes, Hydroxy-ketones and Acetals]. K. VON AUWERS [with H. WISSEBACH] (*Ber.*, 1923, **56**, [*B*], 1672—1682).—

From a consideration of the molecular refractive and dispersive powers of the isomeric and substituted angelicalactones, the conclusion is drawn that it is possible to distinguish Δ^1- from Δ^β-lactones by refraction measurements alone. It is also shown that Δ^1-lactones show smaller exaltations of molecular refractive power than do the corresponding unsaturated open-chain ketones, thus conforming to the general rule that ring-closure tends to diminish exaltations of refractive and dispersive power.

The method of exaltations of molecular refractive and dispersive power is also applied to the determination of the structure of hydroxy-aldehydes and ketones, and it is claimed that by exercising great care in the purification of the compound and the determination of its optical constants, it is possible to distinguish between open-chain and cyclic structures. For example, the spectrochemical evidence is in favour of the cyclic structure $O<\begin{matrix}CHMe-CH_2\\ CH(OH)\cdot CH_2\end{matrix}$ for γ-hydroxy-valeraldehyde. This tendency to ring formation is more marked in the case of hydroxy-aldehydes than with hydroxy-ketones.

Spectrochemical evidence is in favour of the normal structure for diphenylacetaldehyde, and not of the isomeric diphenylvinyl alcohol. H. H.

The Doublet Separations of Balmer Lines. J. C. McLENNAN (*Nature*, 1923, **112**, 166).—Results obtained by the author and G. M. Shrum confirm Sommerfeld's theory of the structure of the lines of the Balmer series. A. A. E.

The Secondary Spectrum of Hydrogen under Various Excitations. MASAMICHI KIMURA and GISABURO NAKAMURA (*Japan. J. Phys.*, 1923, **1**, 85—95).—The authors have examined the effects of various modes of excitation on the secondary spectrum of hydrogen. The results indicate that lines of the secondary spectrum between H_α and H_β are very sensitive to a variation of the mode of excitation, whilst those in the region between H_β and H_γ are generally less affected. One group of lines was emitted strongly in a fine capillary of a discharge tube, whilst another was intense in the wider part of the tube. The intensities of the former were much increased by the application of a heavy condensed discharge or a strong magnetic field, or by increasing the gas pressure. In the light emitted from a glowing cylindrical cathode, lines in the region λ 5000 to λ 5700 were enhanced compared with their intensities in the positive column. Lines included between λλ 5700 and 5950 were similarly enhanced by the electrodeless discharge. Assuming the secondary spectrum to be emitted by molecules, the authors consider that lines of the spark type are emitted by ionised molecules whilst those of the arc type originate in neutral molecules. J. S. G. T.

The Band Spectra and the Electronic Configuration of Nitrogen and Carbon Monoxide Molecules. HANTARO NAGAOKA (*Japan. J. Phys.*, 1922, **1**, 49—57).—A comparison of the

respective band and line spectra of carbon monoxide and nitrogen confirms the suggestion of a resemblance in the electronic configurations of the molecules of these gases, derived from measurements of other physical constants. The author considers that the fourteen electrons associated with the oxygen and carbon atoms in the molecule of carbon monoxide, or with two atoms of nitrogen, are symmetrically arranged in a face-centred cube, whilst the positive nuclei occupy the centre of the cube and are in rapid motion, and give rise to band spectra by reacting on the electrons. Moreover, the transition between stationary orbits is greatly influenced by the molecular motions. The greater complexity of the band lines in the spectrum of carbon monoxide is attributable to the asymmetry of the central nuclei in the molecules of this gas. The configuration described conforms with results deduced from the kinetic theory of gas, on the assumption that two atoms have two electrons in common. J. S. G. T.

Combination Relations and Terms in the Band Spectrum of Helium. A. KRATZER (*Z. Physik*, 1923, **16**, 353—366).—From an analysis of the wave-lengths of the lines contained in the band spectrum of helium in the regions $\lambda\lambda$ 6400, 4546, and 5730 Å. as determined by Curtis (A., 1922, ii, 330) the existence of a number of combination relations between wave-lengths in the respective systems classified by Curtis is definitely established. This result is in accord with the author's theory of the emission of band spectra and contrary to the conclusion of Curtis on this matter. The analysis indicates that the bands $\lambda\lambda$ 6400 and 4546 probably originate in the same system of electrons, the initial conditions of these, in the two cases, being characterised by different oscillation quantum numbers, the higher number being associated with the 4546 band. The band λ 5730 Å. belongs to a different system, characterised by the same end-term as that associated with the two other bands. The various terms are calculated by a general method. It is shown that the moment of inertia of the helium molecule about the line joining the electrons with the nucleus is extremely small, and certainly less than $0{\cdot}1h/2\pi$. J. S. G. T.

The Crossed-orbit Model of Helium. LUDWIK SILBERSTEIN (*Nature*, 1923, **112**, 53; cf. this vol., ii, 400).—An examination of certain regularities observed on application of the spectrum formula previously proposed for helium. A. A. E.

Determination of Spectroscopic Standard Wave-lengths in the Short Wave-length Region. SISIR KUMAR MITRA (*Ann. Physique*, 1923, [ix], **19**, 315—339).—Employing the interferometer method devised by Fabry and Perot, the author has determined the following wave-lengths in the arc spectrum of copper below λ 2374 Å., where standard determinations have hitherto been lacking: 2369·891, 2303·134, 2276·261, 2242·622, 2218·107, 2189·631, 2148·897, 2126·047, and 2112·105 Å. In addition, the standard line λ 2334·816 in the arc spectrum of tin has been determined. In general, experimental values differed from the respective mean

values given by less than ±0·002 Å. and never by more than ±0·003 Å. J. S. G. T.

The Mass-spectrum of Copper. F. W. Aston (*Nature*, 1923, **112**, 162).—The masses ascribed by Dempster (this vol., ii, 640) to the isotopes of copper are improbable, since (*a*) no case is yet known of an element of odd atomic number consisting of more than two isotopes, and (*b*) except in the case of nitrogen; with such elements the more abundant of the two constituents, or both, are of odd atomic weight. By the use of cuprous chloride, the mass-spectrum of copper is found to contain lines at 63 and 65, having the expected intensity ratio of about 2·5 : 1, and not showing any deviation from the whole-number rule. Dempster's lines are possibly due to the presence of zinc as an impurity. A. A. E.

An Experimental Verification of the Theory of Röntgen Ray Spectra, due to a Multiple Atomic Ionisation. A. Dauvillier (*Compt. rend.*, 1923, **177**, 167—169).—The spectrum of iron shows Hjalmar's line $K\beta'$ and the line K_γ (due to two superficial electrons of iron, N_8 and N_9), but not the doublet $K\alpha_3\alpha_4$, when excitation is produced, not by direct bombardment, but by fluorescence (cf. this vol., ii, 243, and Wentzel, this vol., ii, 249). E. E. T.

Structure of the Spectrum of the Neutral Molybdenum Atom. Miguel A. Catalán (*Anal. Fis. Quim.*, 1923, **21**, 213—235).—The flame, arc, and spark spectra of molybdenum are composed of two classes of lines attributable respectively to the neutral and ionised atoms. The lines of the first class, which are fully described, consist of three systems of triplets, with lines of intercombination, and five multitriplets with lines of intercombination between these and the first three systems. A close similarity is shown between the spectra of chromium and molybdenum. G. W. R.

Regularities in the Arc Spectrum of Titanium. C. C. Kiess and Harriet K. Kiess (*J. Washington Acad. Sci.*, 1923, **13**, 270—275).—The arc spectrum of titanium has been analysed with the object of ascertaining the regularities of this spectrum. It is shown that two different sets of multiplets of six or seven lines occur. These sets have respectively the differences 170·1 and 216·7 and are similar to the multiplets of the alkaline-earth metals. There are also multiplets of eleven to thirteen lines with differences 42·0, 62·3, 81·7, and 100·2, similar to the multiplets of manganese, chromium, and molybdenum. The majority of the lines classified belong to King's temperature classes I and II, although a few belong to the classes III and IV (*Astrophys. J.*, 1914, **39**, 139). About 10% of the arc lines of titanium are thus classified. Long tables of the classification are given in the paper. J. F. S.

The Absorption Spectrum of Arsenic Sulphide Sols. A. Boutaric and M. Vuillaume (*Compt. rend.*, 1923, **177**, 259—261).—The experimental values obtained for the absorption spectrum of a solution of arsenic trisulphide made by passing hydrogen

sulphide through a solution of arsenious acid containing 5 g. per litre do not seem to be consistent with any of the theoretical laws. There appears to be an absorption by diffusion which itself accords with Rayleigh's law, but it is accompanied by selective absorption which is probably caused by the reflection of incident rays from the surface of the particles. The latter absorption should, therefore, vary with the extent of the total surface, diminishing for a constant weight of the sulphide when the number of particles decreases with consequent increase in their size. This was verified by experiment, the absorption curve showing less variation from the theoretical value with progressive ripening of the sol. H. J. E.

The Absorption Spectra of the Vapours of Various Quinones. JOHN EDWARD PURVIS (T., 1923, **123**, 1841—1849).

Fluorescence and Photochemistry. R. LEVAILLANT (*Compt. rend.*, 1923, **177**, 398—401).—An investigation of the photochemical reduction or oxidation of fluorescent and other dyes, in very dilute solutions. Uranine in glycerol solution (0·01%) is decolorised under the influence of light, owing to photochemical reduction, the colour reappearing on leaving the solution in contact with air, but not doing so if air is excluded. More concentrated solutions (*e.g.*, 0·2%) are not decolorised in this way.

This phenomenon is fairly general with dilute solutions of colouring matters in polyhydroxy-alcohols (ethylene glycol, glycerol, erythritol, mannitol) or with solutions also containing neutral tartrates, dextrose, etc. Eosin, erythrosin, thiazines, and Meldola's blue show the effect well; but pyronin is much less sensitive. Similarly, the reappearance of the colour, on leaving, is observed in the case of thiazines, eosin, etc., but is less marked with Rose-Bengal and Magdala-red. The reappearance of colour depends to some extent on the solvent used and the final colour is not necessarily identical with the original one.

Many acids (acetic, oxalic, lactic, malic, tartaric, citric, etc.) play the same part as alcohols. Thus a solution of methylene-blue in acetic acid is slowly decolorised, whilst in 0·02% aqueous solutions, in presence of oxalic acid, decolorisation is rapid owing to reduction of the colouring matter (M): $H_2C_2O_4+M=MH_2+2CO_2$. Hydroxylamine and phenylhydrazine hydrochloride play the same part as the above acids.

Photochemical oxidation may also occur, uranine being oxidised in aqueous solution in presence of air, irreversibly, to give a brownish-red decomposition product. In absence of air, an aqueous solution of uranine is not affected by light.

Light is supposed to be absorbed by a molecule of the fluorescent substance, which is raised to the critical state. Simple reversion may occur (with light emission), or the substance, in the highly active state, may undergo reduction (or oxidation). A non-fluorescent substance should be less sensitive to light. In fact, fuchsine, tartrazine, malachite-green, and indigo-carmine, in glycerol solution, are unaffected by light although indigo carmine in aqueous solution, in presence of oxalic acid, is partly reduced and

the rhodamines, although fluorescent, are practically unaffected by light, in glycerol solution. The same lack of generality applies to results obtained on the sensitiveness to heat of solutions of colouring matters of the two types. E. E. T.

Phosphorescence caused by Active Nitrogen. H. KREPELKA (*Nature*, 1923, **112**, 134; cf. Lewis, this vol., ii, 361; Jevons, this vol., ii, 451).—A bright green phosphorescence was observed when aluminium chloride, freshly prepared from aluminium and chlorine in a tube through which nitrogen had been passed, was gradually cooled in nitrogen. In the case of aluminium bromide, phosphorescence was not observed. The phenomenon is ascribed to the activation of some of the nitrogen by the violent reaction of the chlorine left in the tube with the aluminium. A. A. E.

The Minimum Concentration of Luciferin to give a Visible Luminescence. E. NEWTON HARVEY (*Science*, 1923, **57**, 501—503; cf. A., 1915, i, 628; 1917, i, 365, ii, 436; 1918, i, 89).—On oxidation in presence of luciferase, the light emitted from a solution of 1 part of dry *Cypridina* in 4×10^8 parts of sea-water can just be detected by the unassisted eye. This corresponds with a concentration of luciferin between 1 in 4×10^9 and 1 in 4×10^{10}. Attention is directed to the degree and tenacity of the adsorption on glass vessels of substances at such dilution. A. A. E.

The Molecular Scattering of Light in Benzene, Vapour and Liquid. K. R. RAMANATHAN (*Physical Rev.*, 1923, **112**, 564—572).—The intensity of the light scattered by benzene, as liquid or vapour, at right angles to the incident beam has been compared with that scattered by ethyl ether. The results, together with the measurements of the degree of polarisation of the scattered light, are held to confirm the general validity of Raman's views (A., 1922, ii, 603). A. A. E.

Optical Rotation and Atomic Dimension. D. H. BRAUNS (*Physica*, 1923, **3**, 69—75).—The optical rotations of chloro-, bromo-, iodo-, and fluoro-acetyldextrose, -acetylcellose, and -acetylxylose have been compared, and the differences between the specific rotations for the fluoro- and chloro-, chloro- and bromo-, and bromo- and iodo-compounds are found to be nearly proportional to the differences in the atomic diameters found by Bragg. The atomic dimensions thus form an additive element in the rotation.

CHEMICAL ABSTRACTS.

The Kinetics of Photochemical Reactions. P. P. LAZAREV (*Bull. Acad. Sci. Russ.*, 1919, 239—254; cf. A., 1915, ii, 719).—A mathematical study of reversible, non-reversible, and pseudo-reversible photochemical reactions under different conditions of light. CHEMICAL ABSTRACTS.

Photo-decomposition of Nitrosyl Chloride. A. KISS (*Rec. trav. chim.*, 1923, **42**, 665—674).—The formation and decomposition of nitrosyl chloride in white light has been investigated at 0·1°, 18°, 38°, 48°, 58°, and 78° by the method previously employed

(this vol., ii, 237). The results show that the rate of formation of nitrosyl chloride is the same whether the mixture is illuminated or preserved in the dark. The decomposition of nitrosyl chloride under the influence of white light is strictly unimolecular. The temperature coefficient of the velocity constant over the range 0° to 78° is unity. J. F. S.

Spectral Sensitiveness of Silver Bromide and the Influence of Adsorbed Substances on the Sensitiveness. W. FRANKENBURGER (*Z. physikal. Chem.*, 1923, **105**, 273—328).—The photodecomposition of silver bromide has been investigated in respect of its dependence on various factors and an attempt is made to explain the mechanism of the decomposition on the basis of the quantum hypothesis and the modern views on crystal structure. The view of Fajans (A., 1921, ii, 386), that the primary process in the ion lattice of the silver bromide consists in the transference of an electron from a bromine-ion to a silver-ion with the formation of free bromine and silver, is accepted as a working hypothesis. Every change in the normal lattice energy (electrical) must affect the electron transference and consequently the sensitiveness of the silver bromide to a greater or less extent. With the object of confirming and extending these views, the photochemical behaviour of preparations of silver bromide of variously constituted surface have been investigated. The surface has been varied by the adsorption of various substances on it. It has been found necessary to distinguish between chemical sensitisation, which consists in the combination of the liberated bromine by acceptors and so preventing it from setting up the reverse reaction with the liberated silver, and optical or spectral sensitiveness, which consists in the change of the lattice energy brought about by the adsorption of foreign substances on the surface. The following cases have been examined. Pure silver bromide free from moisture in the presence of mercury vapour as acceptor has a spectral sensitiveness commencing between 435 and 410 $\mu\mu$. Silver bromide under an excess of silver nitrate solution, which is to be regarded as silver bromide coated with silver-ions, commences to be sensitive to light at $>620\ \mu\mu$, presumably in the ultra-red. The bromine acceptor in this case is the silver nitrate solution itself. The strong sensitisation here is due to the fact that the adsorbed silver-ions, on electrostatic grounds, are more active acceptors of electrons than the silver-ions from pure silver bromide. Silver bromide under an acid solution of potassium bromine begins to be sensitive to light between 435 and 410 $\mu\mu$. In this case, the silver bromide is coated with excess of bromine-ions and hydrogen-ions, and the bromine acceptors were sulphurous acid and phenylpropiolic acid. From silver bromide under alkaline solutions, a different type of photosensitive system is produced, for here the electron passing to the silver-ion comes, not from the bromine-ion, but from the adsorbed hydroxyl- or oxygen-ion. The decomposition commences here at $>620\ \mu\mu$, possibly in the ultra-red. The great sensitisation in this case is due to the decomposition of the very sensitive silver oxide on the surface. For all preparations

of silver bromide, prepared by any of the methods stated, the decomposition of silver bromide commences between 620 $\mu\mu$ and 560 $\mu\mu$ if silver nuclei are formed. The limiting values of the sensitiveness have been compared with thermochemical data, whereby an explanation of the action of the silver nucleus has been obtained. It is pointed out that certain empirical processes used in the photographic practice bring about an increased sensitiveness of the emulsions by means of a modification of the silver bromide grains. These changes are similar to those mentioned above. As a whole, the results found in the present work with substances free from binding materials are confirmed by those obtained with emulsions.

J. F. S.

Electrostatic Recalculation [on the Photochemical Behaviour of Silver Bromide]. K. F. Herzfeld (*Z. physikal. Chem.*, 1923, **105**, 329—332).—A mathematical treatment of the energy relations of the transference of an electron from a bromine ion to a silver-ion in the photo-decomposition of silver bromide, as put forward by Frankenburger (cf. preceding abstract). J. F. S.

Photochemical Reduction of Zinc Sulphide. André Job and Guy Emschwiller (*Compt. rend.*, 1923, **177**, 313—316).—The darkening of zinc sulphide is due to the formation of free zinc. In order that a specimen should be sensitive to light, it must be phosphorescent and hygroscopic; it is more sensitive the more these conditions are satisfied. The darkening is due to the following series of changes. The preparation of the sulphide, involving ignition, affords a metastable product. Incident radiation raises the metastable molecules to a critical state, and, if the sample be dry, it simply emits radiation and reverts to the previous, metastable, condition. When, however, it has deliquesced slightly, hydrolysis occurs, producing hydrogen sulphide and zinc hydroxide. During illumination, a critical molecule of the sulphide reacts with the hydroxide, giving zinc and sulphurous acid, which with hydrogen sulphide affords sulphur, zinc pentathionate also being produced. The main products are thus zinc and sulphur. E. E. T.

Temperature Coefficients of Reactions in Tropical Sunlight. Nilratan Dhar (T., 1923, **123**, 1856—1861).

Action of Ultra-violet Light on Diketones. C. W. Porter, H. C. Ramsperger, and Carolyn Steel (*J. Amer. Chem. Soc.*, 1923, **45**, 1827—1830).—Under the influence of ultra-violet light, benzil is decomposed at temperatures above 200° into carbon monoxide and benzophenone; diacetyl vapour gives carbon monoxide and ethane, but an aqueous solution of diacetyl yields acetic acid and acetaldehyde. In dilute alcoholic solution, in the absence of air, benzil is partly hydrolysed to benzoic acid and benzaldehyde, but part of it is reduced by the alcohol to benzoin. In aqueous alcohol, in contact with air, it is converted into benzoic acid, which is partly oxidised to salicylic acid. Benzilic acid or its decomposition products, namely, benzpinacol in the absence of air,

together with benzophenone in the presence of air, are never found in exposed solutions of benzil. W. S. N.

A Method of Photographing the Disintegration of Atoms and of Testing the Stability of Atoms by the Use of High-speed Alpha Particles. WILLIAM D. HARKINS and R. W. RYAN (*Nature*, 1923, **112**, 54—55).—The high-speed α-particles from thorium-C' have been employed in Wilson's photographic method. Collisions showing an α-particle deflection up to 165° have been observed, as well as the formation of three branches at the point of collision, a characteristic to be expected if the bombarded atom disintegrates. A. A. E.

Secondary β-Rays produced in a Gas by *X*-Rays. PIERRE AUGER (*Compt. rend.*, 1923, **177**, 169—171).—A study of secondary and tertiary β-rays produced as a result of the incidence of X-rays on various gases diluted with hydrogen (to produce longer rectilinear initial β-ray trajectories). In the case of nitrogen, the β-rays have an angle of 80—100° (for the most part) with the X-rays. With heavier gases (*e.g.*, chlorine), the concentration of secondary rays round the perpendicular direction is less marked. A highly ionised path is seen to start from the same origin as a β-ray, the direction being different. This is due to the less violent loss of a second electron (observed with argon, chlorine, and iodine). The speed of the tertiary ray so produced depends on the nature of the gas, and varies only slightly (about a mean value) with the frequency of the X-rays used. E. E. T.

Some Cases of Analogous Action of Radiation and Ozone on Chemical and Colloidal Reactions. A. FERNAU (*Kolloid Z.*, 1923, **32**, 89—92).—A number of cases are enumerated and discussed in which radiation (ultra-violet, α-ray, X-ray) brings about the same reaction as treatment with ozonised air. Sucrose in neutral, acid, or alkaline solution is inverted when subjected to ultra-violet light; egg-albumin, when exposed to the radiation from radium, is coagulated and ceric hydroxide sols are similarly coagulated. These actions are also brought about when the substances concerned are treated with ozone or hydrogen peroxide. The mechanism of the change is discussed. J. F. S.

Chemical Action of Penetrating Radium Rays. XV. The Dependence of this Action on the Fraction of the Rays absorbed. Reduction of Potassium Persulphate. ANTON KAILAN (*Monatsh.*, 1923, **44**, 35—47).—The decomposition, by penetrating radium rays, of hydrogen peroxide, in acid, neutral, and alkaline solution, and of potassium iodide in acid solution, has been measured in vessels of various shapes and sizes, using different ray-filters. The conclusion previously drawn (A., 1922, ii, 466, etc.), that the action depends on the primary β- and the γ-rays in proportion to the number of ion-pairs produced (or producible) by the fraction of these rays absorbed, is now confirmed, as is also the supposition that the fraction of γ- or secondary rays produced from them is of con-

siderable importance (cf. A., 1922, ii, 106) in connexion with the amount of action produced.

With similarly-shaped vessels, quadruplication of the reaction space is accompanied by an increase of action by 30—40%, owing to secondary effects.

In passing from a neutral solution of hydrogen peroxide to one containing sodium carbonate (present to give a $N/1$-solution), the decomposition effected solely by the rays is not increased in amount. In the reduction of potassium persulphate, the number of molecules reduced is of the same order as that of the ion-pairs produced (or producible) by the absorbed rays. The decomposition of persulphate under these conditions is a direct process, and is not due to interaction with hydrogen peroxide formed (cf. Price and Denning, A., 1904, ii, 247). E. E. T.

Chemical Reactions under the Influence of X-Rays. N. P. Peskov (*Bull. Inst. Polytech. Ivanovo-Voznesensk*, 1923, 7, 119—120).—The chemical action of X-rays on organic compounds is very slight as a rule, owing to the fact that the electrons which cause such reactions are very readily absorbed. It is suggested that the activity of X-rays could be greatly increased if the radiation were generated throughout the mass of the reacting substance; such a generation of X-rays occurs when the substance is mixed with the salts of heavy metals and then exposed to the radiation. Thus the action of X-rays in diminishing the activity of diastase is increased twenty times by adding an insoluble barium salt to the diastase solution; the decomposition of o-nitrobenzyl alcohol is similarly affected. Colloidal solutions of platinum, bismuth hydroxide, and stannic oxide also have such a sensitising effect. G. A. R. K.

Carrying-down of Polonium with Bismuth Hydroxide in Soda [Sodium Hydroxide] Solution. Escher (*Compt. rend.*, 1923, 177, 172—173.—When an acid solution containing bismuth and polonium is treated with an excess of sodium hydroxide, the polonium partly remains in solution and is partly adsorbed by the bismuth hydroxide precipitated. This distribution of polonium between the solid and liquid phases is dependent on the proportion existing between the concentrations of bismuth and sodium hydroxide. E. E. T.

Ionisation of Nitrogen by Electron Impact. H. D. Smyth (*Proc. Roy. Soc.*, 1923, [*A*], 104, 121—133).—The method of investigating ionisation potentials previously used for mercury has been improved and extended to gases. The results obtained with nitrogen show that the ordinary ionisation potential at 16·9 volts corresponds with the production of singly charged molecular ions, N_2^+; doubly charged atomic ions, N^{++}, are produced at $24·1\pm1·0$ volts and singly charged atomic ions, N^+, at $27·7\pm0·8$ volts. These results are interpreted as corresponding with the transitions $N_2 \rightarrow N_2^+$; $N_2 \rightarrow N^{++} + N(\text{or } N^-)$ and $N_2 \rightarrow N^+ + N^+$. This leads to the values of 11 and 18 volts for the first and second ionisation potentials of atomic nitrogen. Further results at higher voltages show the

variation of the relative intensity of the different types of ion with the voltage. In particular, there is a very sharp increase in the proportion of atomic ions between 350 and 400 volts, corresponding roughly with the *K*-limit of 375 volts found by Foote and Mohler ("Origin of Spectra," 1922, p. 195). It was found possible to produce negatively charged molecular ions, but only in very small quantities. No negatively charged atomic ions were observed.

J. F. S.

Ionisation Produced by the Hydration of Quinine Sulphate. (Mlle) Chamié (*Compt. rend.*, 1923, 177, 181—184).—In continuation of previous work, with improved apparatus (cf. this vol., ii, 113), the author has studied the hydration of quinine sulphate (the maximum hydration corresponding with a hydrate containing 4·81% of water), using two methods, carried out under the same conditions: increase of weight and decrease in current passing in an enclosed space. It is found that the curves of the diminution of the ionisation current (at points near that of saturation) are symmetrical with those of weight-increase with respect to the same time axis. E. E. T.

Luminescence of Mercury Vapour under the Action of Low-velocity Electrons. V. I. Pavlov (*Bull. Acad. Sci. Russ.*, 1918, 127—150).—Under the experimental conditions, the minimum *E.M.F.* necessary for visible luminescence of mercury vapour was 8·25 volts. A definite amount of electronic energy was found to be necessary for the excitation of each line of the luminescence spectrum, the lines at 546 $\mu\mu$ and 576·9—579·0 $\mu\mu$ being produced by 8·25 volts and 11·75 volts, respectively. A minimum volumetric density of the electrical energy of the discharge is necessary to start visible luminescence. Chemical Abstracts.

The Relation between the Visible Luminescence and the Ionisation of Mercury Vapour under the Action of Electrons. V. I. Pavlov (*Bull. Acad. Sci. Russ.*, 1918, 1931—1954).—The increase of the initial ionisation by the action of the field of electrical discharge (secondary ionisation) does not present an indispensable part of the luminous discharge. It can be totally suppressed, without influencing the increase of ionisation in the field of the visible luminescence. A variation in the initial ionisation as brought about by different means, although necessary to start a visible luminescence and anomalously to ionise the gas, is not necessary for maintaining the luminosity. A constant mechanism of ionisation of a gas may produce a quite different degree of ionisation, after the first stage of luminescence is reached, when all ionisers develop a far larger efficiency. A working hypothesis concerning the cause of the latter phenomenon is developed. Chemical Abstracts.

The Electrical Conductivity of Molybdenite. A. T. Waterman (*Physical Rev.*, 1923, 21, 540—549).—When a current was passed through a strip of molybdenite perpendicularly to the crystallographic *c*-axis, the relation $i=KV^be^{-a/T}$, where i is the current, V the applied *E.M.F.*, T the absolute temperature, and

b, k, and K are constants, was found to be approximately valid. The value of b is generally about 1·6 and of k, 3000. Two forms of molybdenite, of widely differing conductivity, may possess different structures. A. A. E.

Design and Use of Conductivity Cells for Non-aqueous Solutions. J. LIVINGSTON R. MORGAN and OLIVE M. LAMMERT (*J. Amer. Chem. Soc.*, 1923, **45**, 1692—1705).—A study has been made of the errors inherent in the design and use of conductivity cells containing non-platinised electrodes, when employed for non-aqueous solutions, and the following general conclusions have been drawn. In order to make accurate electrical conductivity measurements of dilute non-aqueous solutions, some comparison solution other than the very dilute aqueous solutions needed should be used, since the latter cannot be kept as free from contamination as the non-aqueous solutions which are to be measured. A solution of potassium chloride diluted with alcohol is suggested as the most convenient comparison solution. The change in resistance with a change in frequency from 500 to 1000 cycles has been measured throughout a wide range of resistances with a number of different cells and types of solutions. The results of Taylor and Acree (A., 1917, ii, 7, 8) have been confirmed, but the difference in resistance for small electrodes does not decrease continuously with an increase in resistance, but passes through a minimum between 5,000 and 10,000 ohms. There is not, as Taylor and Acree state, a minimum resistance above which a cell may be used with accuracy, but an optimum range which may or may not give results sufficiently accurate, depending on the accuracy required and the size of the electrodes, since as the size of the electrodes increases, the range and possible accuracy within the range increase. So choosing the cells that the resistance in them is large is not equivalent experimentally to increasing the size of the electrodes. Cells are designed with the aid of Washburn's equations (A., 1917, ii, 10), which do not change in resistance with a change in frequency and which with the Washburn type A cell cover the range from 2×10^{-3} to 2×10^{-7} reciprocal ohms. The method of cleansing and drying the electrodes has been found to be of far greater importance than any of the other factors involved, the errors from this source alone often being as high as 2—3%. The usual method of cleansing and drying seemed to make the cell, filled with its solution, not a resistance and a capacity, but a voltaic cell which gives the effect of an abnormally high resistance. A method is given for cleansing the cells which has for its underlying principle the production of two electrodes having as nearly as possible the same contact potential when immersed in the same solution; it involves scrubbing the electrodes after any treatment with an acid cleaning mixture and keeping the electrodes short-circuited during all the process of cleaning, drying, and bringing the cell to temperature equilibrium. It is believed that the difference in the potential developed by different electrodes when subjected to the same treatment accounts for the change in resistance with a change in the impressed voltage, and for the fact

that some observers have not been able to eliminate the change by cleansing them thoroughly whilst others have. The term "clean" applied to electrical conductivity cells should be more rigidly defined, if comparable values are to be obtained by different workers.

J. F. S.

Ionisation Potentials of Copper and Silver. A. G. SHENSTONE (*Nature*, 1923, **112**, 100).—Low voltage arcs have been obtained in the vapours of copper and silver. For copper, a voltage of 7·8 was found; for silver, the value was 6·0 volts, with indications of a resonance potential at 3·1 volts. A. A. E.

The Hydrogenation Potential of the Alloxantins. EINAR BILLMANN and HAKON LUND (*Ann. Chim.*, 1923, [ix], **19**, 137—144; cf. A., 1921, ii, 372).—Alloxantin being considered as chemically analogous to quinhydrone, an attempt was made to use it for electrochemical purposes in a similar manner. In measuring the potentials of alloxantin electrodes against hydrogen electrodes, it was found practicable to measure the hydrogenation potential of alloxantin and of tetramethylalloxantin. Details of the experimental work are given; the results obtained show for the former substance a value of 0·3696 volt and for the latter 0·3657 volt, the measurements being made at 18° and under a hydrogen pressure of 760 mm. The influence on the hydrogenation potential of the replacement of hydrogen by methyl is greater in the quinhydrone series than for the alloxantins, but the authors point out that in the case of quinhydrones a transformation of the ring structure is involved.

H. J. E.

Critical Potentials of Thallium Vapour. F. L. MOHLER, PAUL D. FOOTE, and A. E. RUARK (*Science*, 1923, **57**, 475—477; cf. A., 1919, ii, 42).—A recalculation of the previous results, the 1·55 volts collision now being regarded as the first resonance point, gives a value of 6·12 volts instead of 7·3 volts as the ionisation potential of thallium. This potential has been redetermined by Lenard's method, with suitable correction of the applied potentials, and a weighted mean of $6·04 \pm 0·1$ volts obtained, in agreement with 6·08 volts corresponding with $2p_2 = 49264$. A peculiar type of resonance potential (0·96 volt, corresponding with the experimental figure, 1·07 volts) is noted, the resonance collision not being followed by the emission of the corresponding single-line spectrum; a metastable form of thallium is produced. Ionisation potentials of aluminium, gallium, indium, and thallium are predicted, respectively, as follows: $2p_2$:—5·960, 5·973, 5·761, 6·082; $2p_1$:—5·946, 5·871, 5·488, 5·120 volts. Resonance potentials are predicted as follows: $2p_2-2s$:—3·129, 3·060, 3·009, 3·269; $2p_2-3d$:—4·004, 4·294, 4·06, 4·47 volts; $2p_2-2p_1$:—0·014, 0·102, 0·273, 0·962 volt. A. A. E.

Forces at Phase Boundaries. EMIL BAUR and P. BUECHI (*Rec. trav. chim.*, 1923, **42**, 656—664).—The potential differences existent at the boundary of two immiscible liquids, such as amyl alcohol and water, are discussed in connexion with the published researches of Baur and Kronmann (A., 1917, ii, 231) and Wild

(this vol., ii, 53). Measurements of a number of complicated cells containing immiscible liquids are described and the potential set up at the boundary of immiscible liquids is evaluated.

J. F. S.

The Electromotive Polarisation of Platinum. A. V. Pamfilov (*Bull. Inst. Polytech. Ivanovo-Voznesensk*, 1923, 7, 68—79).—The anodic polarisation of platinum and platinised electrodes in normal and decinormal sulphuric acid was studied at different current densities (0·01 to 0·12 ampere per sq. cm.).

With the platinum anode, which was a loop of wire 25 mm. long and 0·4 mm. in diameter and was kept rotating at 300 to 500 r.p.m., the electrode potential rose quickly in the first five minutes, then more slowly, reaching a maximum in ten to twenty minutes at a current density of 0·04 to 0·1 ampere, and two and a half to three hours at 0·01 ampere. After a short interruption of the polarising current, a different potential is observed and in general the numerical values obtained are not constant in different experiments, although the general character of the curves is the same. These numerical values appear to depend greatly on the previous treatment of the electrode under observation (action of oxidising or reducing agents, cathode polarisation, etc.).

With a platinised electrode the maximum is attained more slowly and the results are more constant; short interruptions of the current appear to have no effect on the electrode potential. The difference between the potential of the platinised and the solid electrode is found to be 0·1 to 0·2 volt, not 0·4 to 0·6 as observed by Foerster (A., 1909, ii, 962).

It is suggested that the results are best explained by the interaction of the surface of the electrode with the gas generated in the process of electrolysis, the metal suffering a change from which it recovers only after some time; the question of whether an oxide of platinum or a solid solution of the gas in platinum is formed is left open.

G. A. R. K.

Electromotive Force Measurements with a Saturated Potassium Chloride Bridge or with Concentration Cells with a Liquid Junction. George Scatchard (*J. Amer. Chem. Soc.*, 1923, 45, 1716—1723).—A theoretical paper in which it is shown that the proof of Fales and Vosburgh (A., 1918, ii, 424) that the saturated potassium chloride bridge eliminates liquid junction potentials depends on the assumption that in hydrochloric acid solution the activities of the two ions are equal; the proof of Corran and Lewis (A., 1922, ii, 691) depends on incompatible formulæ for the *E.M.F.* at the two electrodes. An analysis of experimental results indicates that the liquid junction potential with saturated potassium chloride is not more than 0·001 volt for solutions less than 0·1*M*, but that it increases rapidly with the concentration for hydrochloric acid. There is some theoretical confirmation for the assumption that the liquid junction potential with a saturated potassium chloride bridge is independent of the sucrose concentration if the concentration of electrolyte remains constant, but

this substantiation cannot be extended to solutes in general. The ordinary thermodynamic formula for the *E.M.F.* of a concentration cell with transport ignores the transport of water. If this be taken into account, the transport number involved is the true and not the Hittorf number. Emphasis is laid on the fact that activity measurements give the activity of the unhydrated ion. An increase in the fraction of ions not hydrated gives the simplest explanation of the increase of activity coefficients in concentrated solutions. J. F. S.

Effect of Sucrose on the Activities of certain Ions. J. W. CORRAN (*J. Amer. Chem. Soc.*, 1923, **45**, 1627—1636).—By means of *E.M.F.* measurements of potassium chloride concentration cells without transport, containing sucrose, the conclusion drawn in a previous paper (Corran and Lewis, A., 1922, ii, 691), that the potassium- and chloride-ions are soluble in the water of hydration of sucrose has been verified. It has been shown that whereas the transport number of the potassium-ion in sucrose solutions remains constant up to a concentration of 50% sucrose, it appears to increase slightly in 60% and 70% solutions. From a survey of Harned's results (A., 1920, ii, 664), it has been shown that the chloride-ion is soluble in the water of hydration of accompanying kations. This conclusion is therefore analogous to that reached in connexion with sucrose. Measurements of the mean activities of barium chloride, in the presence of sucrose, by means of the cell without transport, have shown that the barium-ion, as well as the potassium- and chloride-ions, is soluble in the water of hydration of sucrose. Since the solubility or otherwise of an ion in water of hydration is of primary importance in determining its true concentration in terms of available water, Harned's extension to any ion of MacInnes' postulate regarding the independent activity of the chloride-ion in solutions of univalent chlorides of the same concentration, is only valid for those ions which are soluble in the water of hydration of secondary solutes (either ions or non-electrolytes) (A., 1919, ii, 385). J. F. S.

Behaviour of Cadmium Amalgam in Relationship to the Weston Normal Element. ALFRED SCHULZE (*Z. physikal. Chem.*, 1923, **105**, 177—203).—The diagram of condition of cadmium amalgam for the concentration range 8% to 15% cadmium, which is of importance for the Weston element, has been subjected to a revision. The situation of the liquidus curve is confirmed by the thermal method and then the composition of the liquid phase is confirmed by analysis. The solidus curve could not be determined by the thermal method, for apparently too little heat is rendered latent in this change, nor was the determination possible by the dilatometric method, which is contrary to the experience of Bijl (A., 1903, ii, 6), nor by means of electrical conductivity determinations. On the other hand, the electromotive behaviour of the amalgams allowed the branching point to be definitely fixed in the temperature region 0° to 25°. These results are in excellent agreement with the *E.M.F.* measurements of Bijl at 25—75°, but at variance with his dilatometric measurements. In agreement with

Smith (*National Phys. Lab.*, Collected Researches, 1910, **6**, 137), it is shown that the branching temperature, in the concentration range examined, lies considerably lower than Cohen has assumed (A., 1920, ii, 581). It is important that this fact is found whether the temperature is rising or falling. According to this, the branching point of the 12·5% amalgam used in the Weston cell lies below 0° so that the assertion of Cohen (*loc. cit.*) with regard to the metastability of the normal element is incorrect. The present result is in keeping with the bulk of the data obtained for the Weston element by the various controlling laboratories. Electrolytic amalgams lead to the same results. Divergences of the *E.M.F.* of elements containing strongly cooled amalgams, as obtained by Smith, can be explained by chemical analysis, for the liquid phase of the strongly cooled amalgams has a different composition from that of the slowly cooled amalgams. Measurements of the electrical conductivity of the 14·07% amalgam in the temperature region where the amalgam consists of two phases, show a remarkably large temperature coefficient. The change in resistance per degree is about 2%, whilst for most other metals it is about 4%. J. F. S.

A Simple Model of a Micro-electrode for Estimation of P_H. GUNTHER LEHMANN (*Biochem. Z.*, 1923, **139**, 213—215).—A micro-electrode is described and figured suitable for the determination of the P_H of a drop of fluid. It works as rapidly as the large electrode and gives values in agreement with the U electrode of Michaelis. H. K.

Gas Electrode. M. KNOBEL (*J. Amer. Chem. Soc.*, 1923, **45**, 1723—1724).—A very convenient form of hydrogen or other gas electrode which reaches the equilibrium value very quickly is described. It consists of a piece of graphite rod 3 mm. in diameter and about 3—4 cm. long which is bored axially to within 6 mm. of the bottom. This is connected with a copper tube of the same diameter by a short length of rubber and electrical connexion between the two made by a copper spiral. The graphite is platinised in the usual way. The measurement is made by leading hydrogen at ½—1 atm. pressure into the tube, when it slowly bubbles from the graphite surface, thus constituting an extremely good electrode. The equilibrium value is reached in one and a half minutes and remains constant and is entirely independent of the pressure outside. J. F. S.

The Action of Silica on Electrolytes. ALFRED FRANCIS JOSEPH and JOHN STANLEY HANCOCK (T., 1923, **123**, 2022—2025).

Electrical Properties of Silicic Acid Sols. W. GRUNDMANN (*Koll. Chem. Beihefte*, 1923, **18**, 197—222).—The change in silicic acid sols has been investigated by means of determinations of the amount of silicic acid carried by an electrical current and by determinations of the reduction of the electrical conductivity of hydrochloric acid in presence of varying quantities of the sol. It is shown that the charge of the silicic acid particles in an hydrochloric acid solution of silicic acid changes when the solution is kept for some

time. In the first few days, the charge becomes more negative and after five to ten days reaches a maximum, after which it becomes more positive. In the case of solutions from 0·0002 to 0·0004*N*-hydrochloric acid, the charge changes its sign twice. The maximum is reached earlier the smaller the concentrations of acid. The sol without the addition of acid exhibits a change toward the positive side. The diminution of the electrical conductivity increases steadily with time and after five to ten days a value is reached which remains steady for weeks if no coagulation takes place. When coagulation commences, the diminution increases very much. The diminution of the electrical conductivity depends on the concentration of the silicic acid, the concentration of the hydrochloric acid, the age of the sol, and the purity of the sol. With increasing age of the sol, the adsorption in concentrated sols decreases slowly, but increases in dilute sols and after a few days a dilute sol may show a larger diminution than a concentrated sol. J. F. S.

Electro-diffusion (Ionic Migration). ALFRED GILLET (*Compt. rend.*, 1923, **177**, 261—263).—Electrolysis of sodium sulphate solution containing sufficient gelatin to form a stiff jelly was effected and after some time the jelly was cut into sections parallel with the electrodes. Each portion was then analysed and the following conclusions were drawn from the results obtained. The current appears to be carried by the kation only, and towards the anode there is a movement, not only of sulphate-ions, but of all the molecules present in the solution. A species of equilibrium is established in which one molecule of sodium sulphate is equivalent to two of sulphuric acid at the anode and three molecules of sodium hydroxide to one of sodium sulphate at the cathode. Numerous secondary effects occur, but it is stated that none of these is sufficient to affect the conclusions to any serious extent. H. J. E.

A Cataphoretic Apparatus for Small Quantities. A. VON SZENT-GYÖRGYI (*Biochem. Z.*, 1923, **139**, 74—76).—A cataphoretic apparatus is pictured and described suitable for small quantities of liquid. It is based on the Landsteiner-Pauli-Michaelis macro-apparatus. H. K.

Magnetic Properties of Gadolinium Ethyl Sulphate at Low Temperatures. L. C. JACKSON and H. KAMERLINGH ONNES (*Compt. rend.*, 1923, **177**, 154—158).—Gadolinium ethyl sulphate, $Gd(SO_4Et)_3,9H_2O$, is an example of a strongly diluted paramagnetic substance. At temperatures from the ordinary one to 14·56° *K*, the Curie Law (K_mT=const.) is obeyed. The susceptibility is independent of the field applied, so that the substance is purely paramagnetic. Further, crystals of gadolinium ethyl sulphate are magnetically isotropic. E. E. T.

Paramagnetism and Atomic Structure. A. DAUVILLIER (*Compt. rend.*, 1923, **176**, 1802—1805).—The author has interpreted the results obtained by Cabrera (A., 1922, ii, 469), assuming that paramagnetism is due to two causes acting singly or together,

(*a*) the presence of surface electrons, and (*b*) of internal electrons in incompletely furnished layers. Such elements as silicon, sulphur, germanium, selenium, tin, and tellurium, although possessing the same surface structure as those of the titanium and chromium type, are diamagnetic by reason of their electro-negative character. In the cases of scandium and copper, agreement with Cabrera's magnetic moments is good, whilst for the rare earths the two symmetrical magnetic moment curves (cerium–europium and samarium–lutecium) are in accordance with the fact that internal dissymmetry is at a maximum in neodymium and dysprosium.

H. J. E.

A Rapidly-constructed, Cheap, Internally-wound Electric Furnace. HUBERT FORESTIER (*Bull. Soc. chim.*, 1923, [iv], **33**, 999—1000).—About 4 m. of nichrome wire are wound on a metal tube, 3—4 cm. diameter, and the coil is covered with a layer of alundum cement 1—2 mm. thick. This is dried, placed in the axis of an asbestos mould about 10—12 cm. diameter, and the annular space filled with quick setting cement. The whole is then surrounded with a layer of about 3—4 cm. of asbestos wool, the metal tube is withdrawn, and the furnace is ready for use. The furnace described may be heated to 1000° in thirty minutes, and cools to 100° in one and a half hours. Its power consumption is about $\frac{1}{2}$ kw. (4·5 amperes at 110 volts). H. H.

Thermoregulator for Electric Furnaces. JEAN SOLARI (*Bull. Soc. chim.*, 1923, [iv], **33**, 1000—1004).—The apparatus described consists essentially of a differential air thermometer with mercury as the moving liquid. One bulb is maintained at a constant temperature and the other is placed in a small auxiliary furnace of copper tube connected in series with the main furnace. The tube containing the mercury is provided with three platinum contacts so arranged in connexion with a resistance and a swinging commutator that automatic regulation of the current passing through the furnace is secured. If Q be the thermal capacity, R the radiating power, and C the conductivity of the tube carrying the heating coil of the main furnace, and q, r, and c the same constants for the small one, then temperature control to within $\pm 5°$ may be obtained by making Q/q very large, R/r very small (but r must not be too great), and C/c very small (c may be very large). H. H.

Theory of the Temperature Variation of the Specific Heat of Hydrogen. E. C. KEMBLE and J. H. VAN VLECK (*Physical Rev.*, 1923, **21**, 653—661).—New empirical formulæ for specific heats between 300° and 2300° K are: for hydrogen, $c_v = 4{\cdot}87 + 0{\cdot}539\times10^{-3}t + 0{\cdot}146\times10^{-6}t^2$; for water vapour, $c_v = 6{\cdot}03 + 4{\cdot}2\times10^{-3}t - 4{\cdot}07\times10^{-6}t^2 + 1{\cdot}95\times10^{-9}t^3$. The following constants of the hydrogen molecule are computed: nuclear spacing, $0{\cdot}488\times10^{-8}$ cm.; moment of inertia, $1{\cdot}975\times10^{-41}$ gm.cm.^{2}; wave-length corresponding with normal vibration, 2·05 μ. A corrected calculation of the rotational and vibrational specific heat of an elastic model of a diatomic gas molecule is presented. A. A. E.

Some Solidification Curves of Binary Systems. MICHELE GIUA (*J. Amer. Chem. Soc.*, 1923, **45**, 1725—1727; JAMES M. BELL (*ibid.*, 1727).—Polemical; Giua answers Bell's criticism of his interpretation of solidification curves of binary systems (cf. Giua, A., 1914, i, 817; Bell, A., 1921, i, 330); to this Bell replies.

J. F. S.

Cryoscopic Measurements with Nitrobenzene. HUGH MEDWYN ROBERTS and CHARLES R. BURY (T., 1923, **123**, 2037—2043).

Sintering: Its Nature and Cause. ROBERT CHRISTIE SMITH (T., 1923, **123**, 2088—2094).

Application of Thermodynamical Principles to the Time Rates of Chemical Changes and Vaporisation. SHIZUWO SANO (*Japan. J. Phys.*, 1922, **1**, 59—69).—By the use of thermodynamic potential functions, a mathematical expression is derived for the law of mass action in a form applicable to the case of concentrated solutions in which electrolytic ions may be present. In the case of the evaporation of a liquid, when the flux of kinetic energy and the effect of viscosity are taken into account, the assumption that the pressure of the vapour evaporating from the liquid is equal to that of the saturated vapour in equilibrium with the liquid phase appears to contradict thermodynamic principles.

J. S. G. T.

Vapour Tensions of Mixtures of Hydrochloric Acid and Water. N. YANNAKIS (*Compt. rend.*, 1923, **177**, 174—175; cf. (Lord) Rayleigh, A., 1903, ii, 59; Bates and Kirschman, A., 1920, ii, 88).—A determination of the boiling-point isotherm (50°) for the above mixtures. Pressures were measured by Regnault's method, as modified by Zawidsky (A., 1901, ii, 6). The composition of liquid and gaseous phases was determined in each case, eleven different mixtures being examined, of hydrogen chloride percentage 0 to 28·7.

E. E. T.

The Analytical Study of Vaporisation. DAMIENS (*Ann. Chim.*, 1923, [ix], **19**, 179—185).—A description of the experimental methods used in the work previously published (this vol., ii, 316). The results obtained show different types of vaporisation phenomena in the cases studied, (*a*) no intermediate compound is formed as in the system tellurium tetraiodide–tellurium, (*b*) one intermediate compound is formed as in the systems tellurium tetrabromide–tellurium and tellurium tetrachloride–tellurium. Here the mean composition of the vapour is that of the intermediate substance, but only when the mixtures heated are within definite composition limits. The rate of vaporisation is at a maximum in the neighbourhood of the point corresponding with the composition of the intermediate compound, but somewhat displaced in the direction of the more volatile of the original substances. The general conclusion is drawn that in a binary system in equilibrium in the solid state, if endothermic reaction between the two original

substances can take place, the vapour given off may have the composition of the resulting substance with or without that of the more volatile of the two original substances. H. J. E.

An Electrical Fuse for a Calorimetric Bomb. P. V. Zolotarev (*Bull. Inst. Polytech. Ivanovo-Voznesensk*, 1923, 7, 117—118).—The usual method of firing the combustible material in the bomb has been improved by using a platinum wire 5 cm. long and 0·5 mm. in diameter fixed in such a way that the flame of the burning substance does not impinge upon it during the process of combustion. A current of known strength is passed through the wire, allowing the necessary correction to be made; a second wire, of the same dimensions, is inserted into the outer circuit of the calorimeter and serves to indicate when a suitable temperature has been attained. It is found that a fuse of this kind does not melt and can be used almost indefinitely. G. A. R. K.

Heat of Formation of Solid Solutions. G. Bruni (*Bull. Soc. chim.*, 1923, [iv], **33**, 907—908).—A reply to Landrieu (this vol., ii, 535). H. H.

Elevation of the Critical Solution Temperature by the Addition [of other Substances]. Carl Drucker (*Rec. trav. chim.*, 1923, **42**, 552—555).—The elevation of the critical solution temperature of aniline–hexane by the addition of various quantities of water, urethane, benzil, benzamide, and thiocarbanilide has been determined. The same quantity has been determined for the binary system carbon disulphide–methyl alcohol by the addition of water, diphenylamine, carbamide, succinic acid, potassium chloride and bromide, sodium iodide, mercuric chloride, and barium chloride. The results show that the molecular elevation of the critical solution temperature is specific for each of the added substances. Reasons for the absence of colligative relationships in this property are discussed. J. F. S.

Special Case of Fictitious Volume Change in Solution Equilibria. Ernst Cohen, Wilhelma A. T. de Meester, and A. L. Th. Moesveld (*Rec. trav. chim.*, 1923, **42**, 779—783).—In the determination of the fictitious volume change, which occurs in the solution equilibrium of the system tetrachloroethane–naphthalene, using the methods previously described (this vol., ii, 537), it has been found that the specific volume is a linear function of the concentration. Such a relationship has not hitherto been observed. The fictitious volume change has been determined in several ways and in this case it is shown to be independent of the solvent employed. J. F. S.

Upper Range of the Quartz Fibre Manometer. Albert Sprague Coolidge (*J. Amer. Chem. Soc.*, 1923, **45**, 1637—1643).—A form of bifilar quartz fibre manometer is described, from which troublesome harmonic vibrations are eliminated. A method is described by which the instrument may be read up to pressures

of 0·1 to 1 mm., depending on the gas used. The method involves calibration over the whole range with a permanent gas and a McLeod gauge at relatively high pressure, or a knowledge of the viscosity of the gas. So extended, the range of the instrument overlaps that of the McLeod gauge, even with easily condensible vapours. It is suggested that the manometer may be used to determine molecular weights of gases at very low pressures.

J. F. S.

The Coefficient of Viscosity of Helium and the Coefficients of Slip of Helium and Oxygen by the Constant Deflection Method. M. N. STATES (*Physical Rev.*, 1923, **21**, 662—671).—For helium, $\eta^{23}=1962{\cdot}3\times10^{-7}$ (probably $\pm0{\cdot}1\%$). The coefficients of slip of helium and oxygen, respectively, are, for the unpolished silver oxide surface, $\zeta^{76}=123\times10^{-7}$, $61{\cdot}1\times10^{-7}$; for the polished surface, 160×10^{-7}, $64{\cdot}5\times10^{-7}$. A. A. E.

Measurements of the Viscosity and Surface Tension of Viscous Liquids at High Temperatures. EDWARD W. WASHBURN (*Rec. trav. chim.*, 1923, **42**, 686—693).—The author describes methods whereby the viscosity and surface tension of very viscous liquids (glasses) may be determined at high temperatures. Viscosity is measured by a modification of Margules's method of rotating cylinders. The cylinders employed were made of hard, dense porcelain, and the apparatus was standardised by means of very viscous solutions of dextrose. It is shown that the viscosity is given by the usual formula $\eta=KW/S$, where W is the weight required to give the rotating cylinder S revolutions per minute, and K is a constant. This constant is only strictly constant up to viscosities of 1,000 poises but for higher viscosities it varies with the viscosity. A curve has been constructed to express this variation by plotting $\log\eta$ against W/S, from which the viscosity can be read directly when the value of W/S is known for any glass. The errors arising from variations of the two cylinders have been discussed and evaluated. The results for a number of glasses are expressed as a series of curves made by plotting $\log\eta$ against the temperature. From the projection of curves from a solid model, a series of *isokoms* (*iso*, equal, *kommi*, gum) are produced for a series of glasses, which give the compositions having the same viscosity.

A new method is described for the measurement of surface tension; this consists in suspending a cylinder of platinum foil by means of a sensitive spiral spring above the surface of the molten glass. The position of a pointer attached below the spring is read by means of a cathetometer. The furnace is then raised by means of a screw until the surface of the glass just touches the cylinder, which is immediately drawn into the glass by the force of surface tension until these forces are balanced by the extension of the spring. The position of the pointer is again read. A constant of the apparatus is required before the results can be evaluated, and this is obtained by means of liquids of known surface tension, such as water, benzene, and specially prepared viscous liquids. The surface tension is plotted on solid diagrams and the curves

are projected to give a series of *isoepitatic* lines. A set of such curves obtained from a series of molten glasses is given in the paper.
J. F. S.

Surface Phenomena in Sucrose Solutions. RAYMOND RENARD BUTLER (T., 1923, **123**, 2060—2065).

Gibbs's Theorem of Surface Tension applied to Sodium Abietate Solutions. RUDOLF LORENZ (*Kolloid Z.*, 1923, **33**, 15—18).—The measured surface tension of solutions of sodium abietate, which have been aged for five hours, have been compared with the calculated surface concentration of freshly diluted solutions of the same salt, obtained according to Gibbs's principle and a remarkable parallelism between the two sets of values obtained.
J. F. S.

Temperature Coefficient of the Molecular Surface Energy of some Substances with Very Long Carbon Chains. RUDOLF SCHENCK and MARIA KINTZINGER (*Rec. trav. chim.*, 1923, **42**, 759—764).—The authors have discussed the temperature coefficient of the molecular surface energy and show that the measurement of this quantity does not allow conclusions to be drawn as to the degree of association of the substances concerned. A normal value for this factor (2·12) allows the conclusion that the substance concerned is normal, but a high value does not necessarily mean that the substance is associated. It is shown that the geometrical form of the molecule, presence of tautomerides, and many other causes in addition to the temperature have a strong influence on the molecular surface energy. The surface tension of *n*-hexacosane, *n*-myricyl alcohol, and *n*-hexacontane has been determined at a series of temperatures from 91·7° to 190·6° by the capillary rise method and the molecular surface energy and the temperature coefficient have been calculated. The following data are recorded: *n*-hexacosane $d^{91\cdot 7^\circ}$ 0·7560, γ (dynes) 24·79, $\gamma(M/d)^{2/3}$ 1529·6 ergs, k (mean) 3·91 ergs; *n*-myricyl alcohol $d^{95\cdot 2^\circ}$ 0·7773, γ 26·17, $\gamma(M/d)^{2/3}$ 1787·0, k (mean) 4·21; *n*-hexacontane $d^{115\cdot 4^\circ}$ 0·7465, γ 6·366, $\gamma(M/d)^{2/3}$ 2621·8, k (mean) 5·46. The high values of k are discussed in connexion with the long carbon chains of these compounds. According to the Baeyer theory these three compounds must be constructed as spirals with 5, 6, and 12 turns, respectively, numbers which are in the same order as the values of k.
J. F. S.

Density of Accumulation in the Adsorption of Silver-ions by Silver Bromide. K. FAJANS and W. FRANKENBURGER (*Z. physikal. Chem.*, 1923, **105**, 255—272).—The adsorption of silver-ions from a solution of silver nitrate of fixed concentration by silver bromide has been investigated by determining the total surface of the silver bromide from the number of particles in a colloidal solution shortly before its coagulation and the amount of adsorbed silver-ions from the divergence between the Mohr and the Gay-Lussac titration methods. It is shown that in the adsorption

equilibrium with a silver-ion solution of the concentration $1 \cdot 8 \times 10^{-5}$ mol./litre in the presence of potassium nitrate, approximately every fourth to every tenth bromine-ion of the silver bromide surface adsorbs one extra silver-ion. J. F. S.

Adsorption. I. Adsorption of Ions by Freshly Precipitated and Air-dried Manganese Dioxide. N. G. CHATTERJI and N. R. DHAR (*Kolloid Z.*, 1923, **33**, 18—29).—The adsorption of silver nitrate, copper sulphate and chloride, ferric sulphate and chloride, calcium chloride and nitrate, strontium chloride, barium chloride, uranium nitrate, nickel nitrate, potassium alum, aluminium sulphate, zinc sulphate and chloride, magnesium sulphate and chloride, cadmium chloride and sulphate, cobalt chloride, manganese sulphate and chloride, cerium nitrate, and thorium nitrate from solution by hydrated manganese dioxide has been investigated under varying conditions. The results show that the larger the valency of the kation the smaller is the adsorption; thus the atomic adsorption is silver 0·0015, barium 0·00033, zinc 0·00023, iron and aluminium 0·0001. These facts are in keeping with the Hardy-Schulze rule. It is also shown that for a given amount of electrolyte the adsorption increases with the dilution, but the adsorption is the same whether a dilute solution is taken or a concentrated solution containing the same amount of dissolved electrolyte and diluted after equilibrium is set up. The adsorbed quantity is not directly proportional to the amount of adsorbent. The influence of time and temperature is exceedingly small. The effect of the addition of a neutral salt on the adsorption is small, but measurable; thus N-sodium chloride has no effect on the adsorption of copper, but ammonium chloride reduces the adsorption. The adsorption of ions is discussed generally. J. F. S.

Adsorption. II. Adsorption of Compounds and Qualitative Analysis. R. DHAR, K. C. SEN, and N. G. CHATTERJI (*Kolloid Z.*, 1923, **33**, 29—31; cf. preceding abstract).—The adsorption of salts by various precipitates used in qualitative analysis has been investigated. It is shown that strontium sulphate adsorbs iron in large quantities, aluminium and chromium to a smaller extent, nickel, cobalt, and copper still less, and mercury not at all. Barium and calcium sulphates adsorb notable quantities of iron; iron, aluminium, and chromium phosphates adsorb detectable quantities of calcium; aluminium, chromium, and ferric hydroxides adsorb measurable quantities of cobalt, nickel, zinc, and cadmium, but do not adsorb silver. Calcium, barium, and strontium carbonates carry down with them magnesium salts whether the precipitation is effected hot or cold. The addition of barium nitrate to a solution of lead sulphate in ammonium acetate gives a precipitate of barium sulphate containing much lead sulphate. The addition of freshly precipitated copper hydroxide to ferric chloride or potassium alum causes the precipitation of iron or aluminium hydroxide with solution of the copper hydroxide, but the precipitate contains some copper. The oxalates of calcium,

strontium, and barium carry down with them iron and magnesium. Iron is carried down by both calcium citrate and calcium benzoate.
J. F. S.

Nature of the Adsorption Process. I. A. FODOR [with R. SCHOENFELD] (*Koll. Chem. Beihefte*, 1923, **18**, 77—128).—From observations on sols of Congo-rubin, Congo-red, night-blue, and alkali-blue it is shown that analogously to the proteins two kinds of cataphoric transference take place side by side, and consequently two types of carriers of electric charges must be present. Of these, one is the enhydrone, the characteristic of which is its migration under a potential drop against water. The other carriers are those which migrate against solutions of electrolytes but not against water; these constitute the ekhydones. Both kinds may be present in definite concentrations. These latter carriers have an increased power of adsorption on charcoal over the first type. J. F. S.

Effect of Hydrogen-ion Concentration on Adsorption of Dyes by Wool and Mordants. O. REINMUTH and NEIL E. GORDON (*Ind. Eng. Chem.*, 1923, **15**, 818).—The adsorption of Orange II and other dyes by alumina and similar mordants is considerably affected by small changes in the hydrogen-ion concentration; there is also sometimes a marked change in colour. In the example quoted, adsorption decreases rapidly as P_H rises from 3·6 to 5·4. The results obtained with wool confirm those given by Briggs and Bull (this vol., ii, 58). E. H. R.

The Physico-chemical Bases of Vital Permeability. III. R. BRINKMAN and A. VON SZENT-GYÖRGYI (*Biochem. Z.*, 1923, **139**, 274—279; cf. this vol., i, 974).—The authors have studied the spreading of capillary active substances on the surface of water in connexion with the theory of nerve conduction. For this purpose, a horizontal tube 1·25 m. long and 2 cm. wide is half filled with pure water of surface tension 74·5. A platinum ring attached to a torsion balance touches the water at one end and the torsion is adjusted to 72·5, so that when the surface tension is lowered by 2 dynes the platinum ring and water become separated. At various distances along the tube, quantities of 0·0001 to 0·001 c.c. of capillary active substances can be dropped on to the water surface by means of a fine pipette operated by a rubber membrane. Records are taken electrically. It was found that methyl or ethyl alcohol, ether, light petroleum, paraffin, glycerol, pyridine, or alkaloids did not spread on the surface in such a way as to free the ring. Hexoic, decoic, oleic, and α-hydroxybutyric acids and sodium oleate spread over the surface with constant velocity and released the ring. Using an alcoholic solution of oleic acid, the minimum quantity of oleic acid required to free the ring was found and this corresponded with a film on the whole surface of 0·2 $\mu\mu$ thickness, or one molecule thick. H. K.

Improvements in the Mode of Measurement of Osmotic Pressure. ARTHUR GROLLMAN and J. C. W. FRAZER (*J. Amer. Chem. Soc.*, 1923, **45**, 1710—1716).—A number of improvements

in the preparation of cells for the measurement of osmotic pressure are described. The pores of cells are filled with some insoluble material which gives additional support for the membrane. The filling material, which is generally magnesium silicate, is produced *in situ* by diffusion of the necessary solutions or electrolytically, and, after washing, the cell is baked at 1000—1450°. The most rapid results are obtained when the membrane is deposited by a modification of the Pfeiffer method instead of by electrolysis. This is carried out by filling the air-free cell with M-copper sulphate, and placing it in a beaker of water until the electrolyte has diffused through the walls. It is then washed on the outside and the water replaced by a M-solution of potassium ferrocyanide and the arrangement left over-night. A cell so prepared will give the equilibrium osmotic pressure in a very few minutes after introducing the solution. It is also shown that a water interferometer serves as the most suitable pressure gauge for the measurement of osmotic pressure. A number of modifications in the construction of such a gauge are described (cf. Adams, A., 1915, ii, 478; Cohen and Bruins, this vol., ii, 118). J. F. S.

Kinetic Theory of the Laws of Osmotic Pressure of Strong Electrolytes. P. Debye (*Rec. trav. chim.*, 1923, **42**, 597—604).—A theoretical paper in which on the basis of the kinetic theory, the author has deduced expressions for the osmotic pressure of strong electrolytes. J. F. S.

Aqueous Solutions. Origin of Osmotic Effects. Camille Gillet (*Compt. rend.*, 1923, **177**, 257—258).—The author claims priority over Armstrong (this vol., ii, 542) and Kling and Lassieur (this vol., ii, 543), but points out that the results obtained by these workers, independently in each case, have considerable corroborative value. He gives a summary of his views and mentions results to which they have led, enumerating researches based on them (cf. A., 1909, ii, 388; 1910, ii, 381; 1912, ii, 1043). H. J. E.

Mutual Solubility Curve of Two Liquids in the Region of the Critical Solution Point. J. E. Verschaffelt (*Rec. trav. chim.*, 1923, **42**, 683—685).—A theoretical paper, in which, making use of the experimental results of Michels (A., 1922, ii, 486) on the mutual solubility of *iso*butyl alcohol and water, the author has shown that the mutual solubility in the region of the critical solution temperature can be represented by an equation of the same type as has previously been employed to express the change of density near the critical point. The formula in the present case has the form $\log(x_2-x_1)=1{\cdot}330+0{\cdot}315\log(t_c-t)$, where x_2 and x_1 are the concentrations of the two co-existing phases at temperature t and t_c is the critical solution temperature. J. F. S.

Investigation of the Molecular Form by Means of Crystalline Liquids. D. Vorländer (*Z. physikal. Chem.*, 1923, **105**, 211—254).—A résumé of fifty-four dissertations published at Halle since 1902. It is shown that the formation of supercooled liquids, in the case of organic compounds, is favoured by those

constitutive influences which oppose the formation of liquid crystals, namely, branched chains, uneven number of side-chain groups, and meta- and ortho-substitution. If the properties of crystalline liquids be taken as the manifestation of molecular arrangement, then in all probability the phenomena of supercooling of amorphous liquids may be taken as being characteristic of a lack of molecular regularity. If the molecules of an amorphous melt are regarded as in motion, then it must follow that linear or symmetrical molecules must more easily produce a space lattice than those containing branched chains or in general an unsymmetrical structure. Other conditions may have an influence on the crystalline arrangement, but the molecular form is of greatest importance in the supercooling phenomena. J. F. S.

Molecular and Crystal Symmetry. T. V. Barker (*Nature*, 1923, **112**, 96; cf. this vol., ii, 388).—A reply to Shearer and Astbury (this vol., ii, 468). A. A. E.

Historical Development of the Idea of the Universality of the Colloidal Condition, together with some Data from the History of the Extension of the Conception Colloidal Condition in Reference to its Compass and Contents. P. P. von Weimarn (*Koll. Chem. Beihefte*, 1923, **18**, 165—196).—An historical discussion of the extent of the domain of colloid chemistry. J. F. S.

Myricyl Alcohol Jellies. E. H. Buchner (*Rec. trav. chim.*, 1923, **42**, 787—789).—The solubility of myricyl alcohol in amyl alcohol and chloroform has been determined at a number of temperatures and the solubility curve constructed. It is shown that the solubility curves after rising rapidly to 40° and 60°, respectively, then rise toward the melting point of myricyl alcohol and do not show anything approaching an horizontal part. This proves that in the liquid state myricyl alcohol is completely miscible with chloroform and amyl alcohol. Consequently, the evidence in favour of the emulsion theory of jelly structure is lost. The experiments show that the jelly of myricyl alcohol is a conglomerate of very fine crystals which retains a large quantity of liquid in the meshes. J. F. S.

Electrolytic Dissociation of Ionisable Colloids. A. Gyemant (*Kolloid Z.*, 1923, **33**, 9—15).—A theoretical paper in which hypotheses concerning the characteristic properties of the dispersed particles of ionisable colloids are put forward, which enable the connexion between the size of the particles and the quantity of the adsorbed ions, and also the electric charge, to be determined. On the basis of this hypothesis, the law of mass action has been applied to weak colloidal acids and bases and the divergence of the dissociation relationships of these substances compared with those of molecular dispersed electrolytes. J. F. S.

Protective Colloids. XIII. *Semen ceratoniæ siliquæ* as Protective Colloid. I. General Colloid Chemical Investigation of Carob Bean Extract. A. Gutbier, E. Locher, and K. Kreidl (*Kolloid Z.*, 1923, **33**, 37—39).—A stable extract of

carob beans may be prepared by crushing the beans, washing repeatedly with cold water, and then extracting 30 g. of the material for two to three days with a litre of water saturated with chloroform, at 50—60°. The extract is amber-coloured and is comparatively stable; an aqueous extract, however, is not at all stable. The extract has powerful reducing properties and decreases in viscosity on keeping. The viscosity increases with increasing concentration, and decreases with increasing temperature; it is unchanged by the addition of dilute hydrochloric acid (0·29%) and by sodium hydroxide (0·29%). The addition of 0·29% of sodium chloride causes a slight increase in viscosity. The colloid is negatively charged and under a potential of 110 volts it migrates to the anode. J. F. S.

Protective Colloids. XIV. Norgine as Protective Colloid. A. Gutbier, E. Sauer, and G. Kröner (*Kolloid Z.*, 1923, **33**, 92—98).—The properties of norgine and its suitability as a protective colloid have been investigated. Norgine is the ammonium sodium salt of laminaric acid and is obtained from seaweed (*Laminaria digitata* and *Saccharinus digitatus*). A full account of the colloidal properties of the substance is given. J. F. S.

Emulsions of Mineral Oil with Soap and Water: The Interfacial Film. Edward L. Griffin (*J. Amer. Chem. Soc.*, 1923, **45**, 1648—1657).—Emulsions of kerosene in solutions of sodium and potassium oleate, palmitate, and stearate have been investigated. The quantity of soap in the interface and in each liquid phase has been determined. The results show that, in an emulsion of a mineral oil with soap and water, part of the soap is hydrolysed, the fatty acid being dissolved by the oil droplets and the free alkali remaining in the aqueous solution. The fatty acids may be prevented from dissolving in the oil by the addition of an excess of alkali. Part of the soap forms unimolecular films round the oil droplets. The average areas occupied by each molecule of sodium oleate, potassium stearate, and potassium palmitate were found to be 48, 27, and 30×10^{-16} sq. cm., respectively. These areas agree rather closely with those found for the corresponding fatty acids in unimolecular films on the surface of water (Langmuir, A., 1917, ii, 19, 525). In the case when sufficient soap is not present to form a unimolecular film, the emulsion is not stable. When an excess of soap is used, this remains in the aqueous solution.

J. F. S.

Adhesion Forces in Solutions. II. Coagulation of Coarse Suspensions. Sergius Wosnessensky (*Kolloid Z.*, 1923, **33**, 32—34; cf. A., 1922, ii, 350).—The sedimentation of suspensions of kaolin, antimony trioxide, and aluminium hydroxide in the presence of a number of electrolytes and mixtures of electrolytes has been investigated. The experiments show that the coagulation of coarse suspensions can only be brought about by the simultaneous action of bi- or ter-valent metals and an alkali hydroxide. The adsorption of the electrolytes on the surface of the suspended particles causes the formation of difficultly soluble hydroxides,

whereby the properties of the suspended particles are entirely changed and this can bring about a change in the cohesive and adhesive forces. The presence of substances which hinder the hydroxide formation disturbs the coagulation. J. F. S.

Rhythmic Banded Film Precipitates on the Surface of Liquids. II. A. JANEK (*Kolloid Z.*, 1923, **33**, 86—89; cf. this vol., ii, 395).—The formation of film precipitates on the surface of semi-solid solutions of gelatin containing potassium dichromate by silver nitrate has been investigated. It is shown that the band formation is independent of the concentration within the limits of the concentration used, 0·03 to 0·30 g. of potassium dichromate in 30 c.c. of 3·3% gelatin solution. The band formation has a definite structure and its thickness increases with the thickness of the gelatin layer on which it is formed, but in thicker layers it is shown to form only on the surface of the gelatin layer. J. F. S.

The Significance of Displacement of Equilibrium. ALBERT COLSON (*Compt. rend.*, 1923, **177**, 184—186).—This law (that of Opposition of Reaction to Action), as far as solubility relationships are concerned (cf. this vol., ii, 543) cannot be verified when the solubility or the heat of solution is small. With concentrated solutions difficulties have arisen owing to the tendency to ignore the volume of the dissolved solute, for this volume may be of the same order as that of the solvent. The classical law can be applied in the case of solutions of ice in alcohol at low temperatures, but fails when the contraction volume (due to ice passing into water) becomes of the same order as that of the alcohol. The author concludes that in a saturated solution the variation of the concentration is neither always, nor exclusively, controlled by the heat of solution, even at a fixed pressure. E. E. T.

The Mass Law and Statistical Equilibrium. WORTH H. RODEBUSH (*Science*, 1923, **57**, 358—359).—It is as fallacious to apply the mass law to too dilute solutions as to too concentrated solutions (cf. Neuhausen, this vol., ii, 396. The precipitated mercuric sulphide probably being in statistical equilibrium with the solution, the absolute number of mercuric- and sulphide-ions per c.c. must be very great). Since ions are shown to exist as such in a crystal, the mechanism of reaction between solids and solutions does not differ from reaction in solution. A. A. E.

The Trajectories of Crystallisation in Chemical Equilibrium Diagrams. N. S. KURNAKOV and S. F. SHEMTSCHUSHNI (*Bull. Acad. Sci. Russ.*, 1918, 1855—1858).—In connexion with results obtained by other authors in experimental work covering the isothermic crystallisation of the mutual system: $2NaCl + MgSO_4 = Na_2SO_4 + MgCl_2$ from aqueous solutions at 25°, it is stated that both the isothermic and isotonic diagrams of equilibrium together with all derived diagrams representing the correlations between composition and properties, may be considered as polyhedra

to which the rule of Euler: α_0(corners)$-\alpha_1$(edges)$+\alpha_2$(faces)$-2=0$, is generally applicable. Polyhedra of this type can be reduced to an open complex tree by removing n lines, where n equals $\alpha_1-\alpha_0+1$, and this reduction may be pushed further until the simple tree of crystallisation of two phases (or two salts) is left. They can also be projected upon the surface of a globe, by drawing lines from the centre of the globe through the corners of the polyhedron. These axes form the invariants of each system, whilst the polyhedric systems projected by them can be treated by means of the theory of algebraic groups. CHEMICAL ABSTRACTS.

Equilibrium in the System of the Four Components Sulphuric Acid, Ammonium Sulphate, Lithium Sulphate, and Water at 30°. G. C. A. VAN DORP (*Rec. trav. chim.*, 1923, **42**, 765—774).—The four three-component systems made up from the four components named in the title have been investigated by Schreinemakers and Cocheret (A., 1906, ii, 424) and van Dorp (A., 1914, ii, 114). The results of these investigations together with some new solubility determinations with the four components are combined and the complete equilibrium diagram of the system is constructed. J. F. S.

Equilibrium between Water, Potassium Chloride, Potassium Nitrate, Calcium Chloride, and Calcium Nitrate. JEAN BARBAUDY (*Rec. trav. chim.*, 1923, **42**, 638—642).—The heterogeneous equilibrium $Ca(NO_3)_2+2KCl \rightleftharpoons 2KNO_3+CaCl_2$ has been investigated. Solubility equilibria of the ternary systems $H_2O-KCl-KNO_3$, $KCl-CaCl_2-H_2O$, $H_2O-KNO_3-Ca(NO_3)_2$, and $H_2O-CaCl_2-Ca(NO_3)_2$ have been determined at 30° and tabulated and the quaternary equilibria $KCl-Ca(NO_3)_2-H_2O$ and $CaCl_2-KNO_3-H_2O$ investigated by the synthetic method at the same temperature. The whole of the results have been combined in an equilibrium diagram. J. F. S.

Equilibria of Tungsten and Tungsten Oxides with Hydrogen and Water Vapour. W. REINDERS and A. W. VERVLOET (*Rec. trav. chim.*, 1923, **42**, 625—631).—The authors have investigated the equilibria $WO_2+2H_2 \rightleftharpoons W+2H_2O$; $W_2O_5+H_2 \rightleftharpoons 2WO_2+H_2O$ and $2WO_3+H_2 \rightleftharpoons W_2O_5+H_2O$ at a series of temperatures and have compared their results with the widely diverging results of Chaudron (A., 1920, ii, 379), of Wöhler and Prager (A., 1917, ii, 455), and of Wöhler and Balz (A., 1921, ii, 633). In the case of the equilibrium between tungsten and the dioxide, it is found that equilibrium is set up at 685° in the presence of 74% of hydrogen, at 830° in the presence of 65% of hydrogen, and at 920° with 58% of hydrogen. These values are all somewhat higher than those found by the authors named above. In the case of the equilibrium between the blue oxide (W_2O_5) and the dioxide, equilibrium is set up at 830° in the presence of 43% of hydrogen and at 700° with 55% of hydrogen. The value found at 830° is identical with that of Chaudron but higher, as is also the value at 700°, than the other results. In the third case, blue oxide–tungsten trioxide, the results are widely

divergent, and it seems impossible to give the so-called blue oxide a definite composition. The blue compounds obtained in the present work vary in composition from $WO_{2\cdot75}$ to $WO_{2\cdot72}$, so that no trustworthy figures for this equilibrium can be quoted. J. F. S.

The Acid-Base Equilibrium in Simple Two-phase Systems. CECIL D. MURRAY (*J. Biol. Chem.*, 1923, **56**, 569—591).—By combining the distribution law with the law of mass action, equations have been developed which relate the distribution of a weak acid in a two-phase system with the P_H of the aqueous phase. The effect of the second (non-aqueous) phase on the buffer value of the weak acid is also considered. Various possible applications of the equations are discussed. E. S.

Ternary System Sucrose–Citric Acid–Water. Theory of Edible Ices from the Point of View of the Phase Rule. ROBERT KREMANN and HERMANN EITEL (*Rec. trav. chim.*, 1923, **42**, 539—546).—The authors have constructed freezing-point diagrams for the binary systems, water–sucrose and water–citric acid and for the ternary system water–sucrose–citric acid. It is shown that the eutectic between citric acid hydrate and ice lies at $-11{\cdot}4°$ to $-11{\cdot}6°$ and contains 46·5% of citric acid. The eutectic between sucrose and water cannot be obtained directly from the freezing curve, but from the intersection of the freezing curve and the solubility curve the eutectic is shown to lie at $-14{\cdot}5°$ and to contain 62·5% of sucrose. The solubility of sucrose has been determined at various temperatures and the following values expressed in g./100g. of solution are recorded: 0°, 64·2; 5°, 64·9; 10°, 65·6; 15°, 66·3; 20°, 67·1; 25°, 67·9, and 30°, 68·7. The freezing-point curves of the ternary system have been determined for four concentrations of citric acid and the spatial model has been constructed. J. F. S.

The Velocity Constant of a Unimolecular Reaction. JAMES RICE (*Phil. Mag.*, 1923, [vi], **46**, 312—320).—From a statistical investigation of interactions between molecules represented by a mechanical model in which two bodies are bound by a quasi-elastic force, the author derives an expression for the velocity constant κ of a unimolecular reaction in the form $\kappa = kTe^{-\mu\phi(c)}/\int_0^c\int_{-\infty}^{\infty} e^{-\mu\epsilon}dqdp$, where the double integral in the denominator is proportional to the number of undissociated molecules, the number of these included in the phase extension q, p to $q+dq$, $p+dp$ being represented by $Ae^{-\mu\epsilon}dqdp$, where A is a constant. The energy associated with the mechanism referred to is given by $\epsilon = p^2/4a + \phi(q)$, where a is in general a function of q. c is the critical distance of separation of the components, beyond which the potential energy associated with the molecular model either decreases or remains constant. k and T have their customary significance. It is shown that by suitable modification of the expression derived for κ, in any one of several ways suggested by quantum considerations, formulæ approximating to that derived empirically by Dushman (A., 1921, ii, 315) for the velocity constant of a unimolecular reaction, in the form $\kappa = \nu e^{-h\nu/kT}$ may be obtained. Thus, assigning to the molecular model the

properties of a harmonic oscillator, the expression $\kappa=2\nu e^{-h\nu/kT}$ is derived. A more general expression in the form $\kappa=(2n/n-1)\nu' e^{-h\nu'/kT}$, where $\nu'=(n-1)\nu$, is also derived. J. S. G. T.

The Velocity of a Unimolecular Reaction. A. McKeown (*Phil. Mag.*, 1923, [iv], **46**, 321—327).—Applying Einstein's conception of the mechanism of energy exchanges between molecules and radiation (*Physikal. Z.*, 1917, **18**, 121) and employing Christiansen's postulation of the existence of "stationary states" (this vol., ii, 62) regarded respectively as the normal, n, and the activated, m, which are such that $\epsilon_m-\epsilon_n=h\nu$, the symbols having the customary significance, the author deduces an expression for the velocity k_1 of a unimolecular chemical change in the form $k_1=p_m/p_n\,.\,\nu e^{-h\nu/kT}$, where p_n and p_m denote the respective *a priori* probabilities of the states n and m. The expression agrees formally with Dushman's empirical relation $k_1=\nu e^{-h\nu/kT}$ (A., 1921, ii, 315). J. S. G. T.

Velocity of a Unimolecular Chemical Reaction. W. C. McC. Lewis (*Phil. Mag.*, 1923, [vi], **46**, 327—329).—In a previous paper (A., 1920, ii, 100), the author deduced an expression for the velocity of a unimolecular change which involved a refractive index term, and afforded a value of the velocity only one ten-millionth of that actually observed. The discrepancy is removed in the present communication by assuming that the oscillator involved is capable of drawing on the radiation present in a volume which is great compared with the magnitude attributed to the oscillator itself. Along these lines, it is shown that the velocity, κ, of an unimolecular change is given by $\kappa=8e^{-h\nu/kT}d\nu$, where the symbols have the customary significance, and where $d\nu$ represents the width of the band or range of frequencies in the neighbourhood of ν which the molecule is capable of absorbing. Assuming, in agreement with the results of Ribaud (*Compt. rend.*, 1920, **171**, 1134), that $d\nu=0{\cdot}17\nu$, the author obtains $\kappa=8\times0{\cdot}17\nu e^{-h\nu/kT}$, in close agreement with Dushman's empirical formula $\kappa=\nu e^{-h\nu/kT}$ for the velocity of a unimolecular change (A., 1920, ii, 315). J. S. G. T.

Temperature of Ignition of Electrolytic Gas. H. von Wartenberg and H. Kannenberg (*Z. physikal. Chem.*, 1923, **105**, 205—210).—The ignition temperature of electrolytic gas (hydrogen and oxygen) has been determined under conditions which eliminate the possibility of a catalytic action of the walls of the apparatus, by bringing together the separately heated gases. The fall of temperature of the gases due to radiation was evaluated in two ways and the ignition temperature at 1 atm. pressure found to be 642°, or 52° lower than the value found by Dixon (T., 1899, **75**, 600). The temperature of ignition of carbon disulphide vapour in oxygen is found to be 236°, a value identical with Dixon's value. J. F. S.

The Propagation of the Explosive Wave. P. Laffitte (*Compt. rend.*, 1923, **177**, 178—180).—A study of the propagation of waves of combustion and explosion in spherical vessels containing a mixture of carbon disulphide (1 vol.) and oxygen (2 vols.) (cf. this vol., ii, 472). Ignition of the mixture was effected in two ways:

(1) By means of an electric spark at the end of a narrow tube projecting into the centre of the vessel. In this case, the explosive wave sent down the tube became a wave of combustion in the main vessel. (2) By means of mercury fulminate, detonated in the centre of the vessel. In this case, an explosive wave was set up instantaneously, with a velocity of 1800 metres per second.

E. E. T.

The Simultaneous Combustion of Hydrogen and Carbon Monoxide. R. T. HASLAM (*Ind. Eng. Chem.*, 1923, **15**, 679—681).—In the combustion of coal any hydrocarbons are consumed first and the combustible gases remaining are hydrogen and carbon monoxide. In a series of gas analyses of samples taken at various points along a 12·2 m. flue into which the products of combustion of a coal fire burning with excess of air passed, the conditions are suitable for a determination of the relative velocity of combustion of those two gases. These velocities are—$dCO/dt=k_1(CO)^m(O_2)^n$ and $d/dt\cdot(H_2)=k_2(H_2)^r(O_2)^s$.

If it is assumed that $n=s$ and $m=r=1$, the relative velocity constant $k_1/k_2[\log(CO)_1-\log(CO)_2]/[\log(H_2)_1-\log(H_2)_2]$.

The experimental data obtained as above give concordant figures for the quantity k_1/k_2 on these assumptions as regards the values of m, n, r, s, but not on other assumed values. It is therefore deduced that these assumptions are correct, *i.e.*, that both reactions are termolecular, $2CO+O_2=2CO_2$ and $2H_2+O_2=2H_2O$, and that the relative rate of combustion $k_1(CO)/k_2(H_2)=0·35$ (approx.). These conclusions, which are contrary to those of various other investigators, are limited to the case of combustion of a gas mixture under the conditions above described.

C. I.

The Relative Influences of Water Vapour and Hydrogen upon the Explosion of Carbon Monoxide–Air Mixtures at High Pressures. WILLIAM A. BONE, DUDLEY M. NEWITT, and DONALD T. A. TOWNEND (T., 1923, **123**, 2008—2021).

Velocity of the Action of the Halogens, Oxygen and Nitrogen, on Metals, Determined by the Colours of the Surface Films. G. TAMMANN (*Rec. trav. chim.*, 1923, **42**, 547—551).—The velocity with which gases react with finely polished metal surfaces may be followed by observation of the colours of the metal surfaces. It is necessary to ascertain the thickness of the air layer which will produce the same colour, and this air thickness is proportional to the thickness of the film. Thus air thicknesses of 140 $\mu\mu$, corresponding with straw-yellow, to 1000 $\mu\mu$ corresponding with the fourth order red, can be observed which in the case of the action of iodine on silver correspond with from forty-three to three hundred and thirteen molecules of silver iodide. The rate at which the film thickens in the case of the action of the halogens on silver, copper, and lead follows the law $y^2=2pt$, where y is the thickness of the layer, t the time, and p a constant. In the case of silver iodide, the value of p is really constant between 15° and 145°; at the latter temperature it increases to three times its original value

and then becomes constant again to 185°. This jump in the value occurs at the transition point of silver iodide. In the case of the action of nitrogen or oxygen on iron and cerium, the rate at which the film increases in thickness is given by $y=[\log_e(t+a)-\log_e a]/b$ at constant temperature, where y is the thickness, t the time, b the fraction by which the concentration of the gas is reduced in the length, dy, of the film, and a is a constant. The authors have calculated the time necessary for the formation of a visible film when oxygen acts on dry metals at 15°. The following values are recorded: lead, ninety years; zinc, 31×10^3 years; cadmium, 19×10^5 years; copper, 6×10^8 years; tin, 36×10^8 years; iron, 25×10^{17} years, and nickel 475×10^{17} years (cf. A., 1920, ii, 248; 1922, ii, 852). J. F. S.

Hydrolysis of Potassium Hydrosulphide in Aqueous Solution. JARL A. WASASTJERNA (*Soc. Sci. Fennica Com. Phys.-Mat.*, 1923, **1**, No. 39, 1—15).—The rate of hydrolysis of ethyl acetate at 25° by solutions of potassium hydrosulphide of various concentrations has been determined with the object of ascertaining the degree of hydrolysis of potassium hydrosulphide. Two new methods of analysing the reacting system at any given moment are described and have been used in the present work. The hydrolytic constant is found to be $10{\cdot}5\times10^{-8}$, and from this value the first dissociation constant of hydrogen sulphide is found to be $7{\cdot}8\times10^{-8}$. Combining the present value of the dissociation constant for 25° with that found by Walker and Cormack for 18° (T., 1900, **77**, 5), the heat of dissociation of hydrogen sulphide is found to be -7700 cal., whilst the value calculated from thermochemical data is -6500 cal. Potassium hydrosulphide, by its presence, reduces the velocity of hydrolysis of ethyl acetate. This effect is about three-quarters of that produced by a corresponding amount of potassium chloride. With very large concentrations of potassium hydrosulphide, the degree of hydrolysis falls very much below the value calculated. J. F. S.

Hydrolysis of Potassium Monosulphide. JARL A. WASASTJERNA (*Soc. Sci. Fennica Com. Phys.-Mat.*, 1923, **1**, No. 40, 1—24).—The velocity of hydrolysis of ethyl acetate by solutions of potassium monosulphide has been determined at 25° with the object of determining the degree of hydrolysis of this salt. The course of the saponification was followed by measuring the change of either the refractive index or the electrical conductivity with time, and corrections were introduced for the neutral salt action of the sulphide. The hydrolytic constant is found to be 15 at 0° and a $0{\cdot}833N$-solution of potassium sulphide is shown to be hydrolysed to the extent of 95%. The second dissociation constant of hydrogen sulphide has been calculated from the results and the value 6×10^{-17} found. From the temperature coefficient of the hydrolytic constant the heat of dissociation of the HS′-ion has been calculated. The result of this calculation, which is somewhat uncertain, is $HS' \longrightarrow H^{\cdot}+S''-18{,}000$ cal. J. F. S.

Saponification of Fats. Influence of the Adsorption of the Emulsifier at the Boundary of Fat and Water Phase on the Saponification Velocity in Boiling Emulsions. J. P. TREUB (*Rec. trav. chim.*, 1923, **42**, 556—567).—A theoretical paper in which it is shown that in the saponification of fats with dilute mineral acids and stearo-naphthalene sulphonic acid as emulsifier (Twitchell's process) the increase of the surface of contact between the fat and the aqueous solution alone cannot explain the influence of the emulsifier on the velocity of reaction. An equation is deduced showing that the emulsifier increases the concentration of the hydrogen-ions at the interface also, and consequently the saponification velocity per unit area of surface of contact. By the increase of the surface of contact and the increase of the hydrogen-ion concentration at this surface, the influence of the Twitchell emulsifier is explained. From the equation deduced, it appears that the emulsifier repels the mineral acid from the boundary of fat and water. Addition of mineral acid cannot therefore increase proportionally the saponification velocity, a deduction in complete accord with fact. Analogous considerations on the saponification with lye show that the abnormal decrease of the saponification velocity near the end of the reaction is due to the repulsion of the hydroxyl-ions from the surface of contact by the adsorbed soap. It appears therefore that the emulsifiers used in saponification in acid media increase both surface of contact between fat and water phase and saponification velocity per unit area of this surface; in saponification in alkaline media, however, the soap formed increases the surface of contact but decreases the saponification velocity per unit area.

J. F. S.

Speed of Reaction in Concentrated Solution and the Mechanism of the Inversion of Sucrose. II. GEORGE SCATCHARD (*J. Amer. Chem. Soc.*, 1923, **45**, 1581—1592; cf. A., 1922, i, 230).—A theoretical paper in which a kinetic interpretation of activity is given which justifies the expression of velocity of reaction in terms of activities and demands that the velocity so expressed be defined as mols. transformed in 1 mol. of all components. This interpretation offers a possible explanation of the effect of salts on the velocity of reaction. The expression of Brönsted (A., 1922, ii, 699) must be modified for concentrated solutions. An analysis of experimental work shows that it is of little value for determining the relation of the velocity of reaction to the viscosity. The kinetic theory, however, demands that the velocity of reaction should be independent of the viscosity. These conclusions lead to the formula for the inversion of sucrose previously put forward (*loc. cit.*) when the concentration of electrolyte is unchanged. The experimental measurements cannot serve as a criterion for choice between the various hypotheses of the mechanism of the reaction, for the difference in agreement between the various formulæ is too small. Any interpretation of the experiments depends on the assumption that the liquid junction potential with saturated potassium chloride is independent of the sucrose concentration.

interpreted by the formula previously put forward (*loc. cit.*), the velocity of inversion catalysed by hydrochloric acid adds confirmation to the statement that six molecules of water react with each molecule of sucrose. The agreement is not quite so good as with sulphuric acid. J. F. S.

Influence of the Speed of Stirring on the Solution of Magnesium in Acids. M. CENTNERSZWER (*Rec. trav. chim.*, 1923, **42**, 579—584).—The rate of solution of magnesium at 25° in $N/8$-hydrochloric acid has been determined under various conditions of stirring. A few experiments are also described on the rate of solution in $N/8$-sulphuric acid or $N/4$-hydrochloric acid when the magnesium is rotated. The experiments show that velocity constant increases proportionally with the rate of stirring the solution. The solution takes place more rapidly when the metal is rotated in the opposite direction to the solution. J. F. S.

The Geometrical Arrangement and Chemical Reactions of the Atom. H. J. PRINS (*Chem. Weekblad*, 1923, **20**, 402—403).—A criticism of Hermans (this vol., i, 767). The present theories of valency and structure explain many otherwise unrelated and apparently contradictory phenomena, and should not too lightly be condemned. S. I. L.

The Model of the Neutral Helium Atom. A. SOMMERFELD (*J. Opt. Soc. Amer.*, 1923, **7**, 509—515).—The model of the neutral helium atom originally proposed by Bohr (A., 1913, ii, 688, 943) and that proposed by Kemble (A., 1921, ii, 478) afford calculated values of the ionisation potential of helium which do not agree with the experimental value, 24·5 volts. Moreover, the models represent helium as being paramagnetic. The author discusses the quantum-relativistic dynamics of a model comprising two electrons moving in opposite senses in two coplanar Keplerian elliptic orbits about a common nucleus. The quantum numbers employed in the analysis refer, not to the single electrons, but to the system as a whole. This model conforms with the diamagnetic character of the neutral helium atom, and with the possibility of the existence of doubly-ionised helium atoms, as found by Millikan (*Physical Rev.*, 1921, **18**, 56). Also, it affords a correct value of the ionisation potential. In general, it appears to be impossible that there should exist in the interior of every atom a system possessing angular momentum and magnetic moment, such as Bohr's model of the K-shell. J. S. G. T.

Electron Valency Theories and Stereochemistry. SAMUEL SUGDEN (T., 1923, **123**, 1861—1865).

Note on the Theory of Free Rotation. THOMAS MARTIN LOWRY (T., 1923, **123**, 1866—1867).

The Octet Theory of Induced Alternate Polarities; the Domains Occupied by Octet-stable and Octet-unstable Centres. RONALD FRASER and J. E. HUMPHRIES (*Phil. Mag.*, 1923, [iv], **46**, 331—334).—The authors seek to vindicate their

interpretation of Lapworth's principle of induced alternate polarities, in which they postulate an electron transference between stable and unstable octets as the necessary accompaniment of the manifestation of such polarities, by considering the domains occupied by stable and unstable centres attached to the benzene nucleus in the case of various chlorobenzenes. In accordance with the view expressed, it is shown that, in every case, the introduction of an octet-stable chlorine centre causes an increase in the average volume of the chlorine atom, whilst an octet-unstable chlorine causes a decrease. Moreover, it is shown that the average volume of the chlorine atom in *m*-dichlorobenzene is about 3% greater than the largest value characterising the poly-substituted chlorobenzenes. J. S. G. T.

Chemical Constants of Diatomic Gases. J. R. PARTINGTON (*Phil. Mag.*, 1923, [iv], **46**, 329—330).—In a recent paper (A., 1922, ii, 839), the author deduced the expression $\log_e m^{5/2} r^2 2^{7/2} \pi^{7/2} k^{7/2}/h^5$ for the chemical constant of a diatomic gas consisting of molecules composed of two like atoms. A similar expression, viz., $\log_e m^{5/2} r^2 2^{9/2} \pi^{7/2} k^{7/2}/h^5$ deduced by Sackur (A., 1913, ii, 128), is considered by the author to be in excess of the correct value by $\log_e 2$. J. S. G. T.

The Ammonium Chloride Problem. A. SMITS (*Rec. trav. chim.*, 1923, **42**, 826—829).—A discussion of the effect of intensive drying of ammonium chloride. J. F. S.

A Pressure Regulator for the Quantitative Measurement of the Velocity of Filtration. WERNER RATH (*Kolloid Z.*, 1923, **33**, 109—111).—A manostat is described by which the pressure may be kept at any desired pressure less than atmospheric during a filtration. J. F. S.

Apparatus for the Continuous Extraction of Solutions by Means of Solvents without the Application of Heat. M. JAVILLIER and L. DE SAINT-RAT (*Bull. Soc. chim.*, 1923, [iv], **33**, 996—999).—Continuous extraction of an aqueous solution is obtained by withdrawing the heavier extracting solvent from below and causing it to fall in a stream of drops through the lighter layer to be extracted. In the case where the solvent used is lighter than the solution to be extracted, it is the latter which is circulated. [See *J.S.C.I.*, 1923, **42**, 868A.] H. H.

Dschâbir and Geber. ERNST DARMSTAEDTER (*Chem. Ztg.*, 1923, **47**, 621—622; cf. Holmyard, this vol., ii, 148; Partington, *ibid.*; Lippmann, this vol., ii, 314).—Geber and Dschâbir are considered to be two distinct individuals; the Arabic manuscripts of the latter are, in fact, believed to have no connexion with Geber or the "Summa perfectionis." Alchemical writings ascribed to Avicenna are stated to contain passages from the "Summa perfectionis." A. A. E.

Inorganic Chemistry.

The Hydration of Hydrogen-ions. J. Baborovský (*Chem. Listy*, 1923, **17**, 170—171; cf. A., 1922, ii, 816).—The mass m_2 of the hydrogen gram-ion in aqueous solution is calculated from the equation $m_1u_1\eta_1 \doteq m_2u_2\eta_2$, where m_1 is the mass of a gram-ion of hydrogen in gaseous hydrogen, u_1 and u_2 the velocities of hydrogen-ions in hydrogen and water, respectively, and η_1 and η_2 the viscosities of hydrogen and of water. The values so obtained for m_2 correspond with 0·66 molecule of water in one case and 0·83 molecule in another per hydrogen-ion, the correct value being probably 1 molecule.

R. T.

Relative Determination of the Atomic Weight of Chlorine in Bamle Apatite. Margot Dorenfeldt (*J. Amer. Chem. Soc.*, 1923, **45**, 1577—1579).—The paper describes work undertaken to ascertain whether the chlorine contained in an old mineral, which has not been in contact with water, contains the two isotopes of chlorine in the same proportion as in ordinary chlorine obtained from sodium chloride. The method of work consisted in determining the specific gravity of saturated solutions of ordinary sodium chloride with that of solutions of sodium chloride prepared from Bamle apatite, using a pyknometer of the type previously adopted by Fajans and Lembert (A., 1917, ii, 472) for a similar purpose. The specific gravity at 18° is found to be the same for both samples. The solubility of both specimens is found to be identical in the two cases, namely, 26·357%. Consequently, the author concludes that the chlorine isotopes in Bamle apatite occur in the same proportion as in ordinary sodium chloride.

J. F. S.

The Kinetics of Chlorate Formation. A. V. Pamfilov and (Mlle) O. S. Fedorova (*Bull. Inst. Polytech. Ivanovo-Voznesensk*, 1923, **7**, 79—84).—The electrolytic formation of sodium chlorate from the hypochlorite is greatly favoured by the addition of a dichromate or free chromic acid. The acceleration of the reaction is observed in strongly acid as well as feebly acid solution, and it is shown that although rather considerable quantities of dichromate have to be added, the latter functions as a true catalyst, the initial and final amounts remaining the same.

G. A. R. K.

Activation of Oxygen. W. P. Jorissen (*Rec. trav. chim.*, 1923, **42**, 855—858).—The author directs attention to a case similar to the atmospheric oxidation of arsenite in the presence of sulphite. A mixture of benzaldehyde and acetic anhydride is oxidised quantitatively to a benzoyl acetyl peroxide by air or oxygen in the presence of sand, $2Ph{\cdot}CHO + O(COMe)_2 + 2O_2 \longrightarrow H_2O + 2COPh{\cdot}O_2{\cdot}COMe$. In this case, the quantity of oxygen taken up is twice as large as that taken up by benzaldehyde in its oxidation to benzoic acid and equal to that taken up in the oxidation of benzaldehyde in the presence of indigo.

J. F. S.

Production of Sulphuric and Hydrochloric Acids from Sulphurous Acid and Chlorine. BERNHARD NEUMANN and FRANZ WILCZEWSKI (*Z. angew. chem.*, 1923, **36**, 377—381).—Measured volumes of sulphur dioxide and chlorine are brought together in the presence of water or, preferably, of strong hydrochloric acid, which is maintained in the form of a spray. As the proportion of sulphuric acid produced increases, the density of the acid mixture rises until, at *d* 1·6, the hydrochloric acid has been almost completely eliminated. The sulphuric acid always contains a considerable proportion of dissolved sulphur dioxide, even if chlorine is added in excess, but either of these gases can be removed by blowing air through the acid. The reaction proceeds quantitatively if sufficient water is present, its velocity being very considerably increased by raising the temperature. The sulphuric acid formed is of 66—88% strength, and the hydrogen chloride is absorbed in the usual manner. Sulphur trioxide is not obtainable according to the equation $SO_2+Cl_2+H_2O=SO_3+2HCl$, the product being sulphuric acid. [Cf. *J.S.C.I.*, 1923, **42**, 827A.] W. T. K. B.

Sulphamide. WILHELM TRAUBE and EMIL REUBKE (*Ber.*, 1923, **56**, [*B*], 1656—1663).—Sulphamide absorbs 1·4 molecular proportions of dry ammonia at +20°, 3·0 molecular proportions at 0°, and 5·4 molecular proportions at −20°. The product so formed has an electrical conductivity about 150 times that of a 4*N*-aqueous solution of sulphamide. Furthermore, a 4*N*-aqueous solution of sulphamide-ammonia has a conductivity twenty-five times that of a 4*N*-solution of ammonia alone. It is therefore suggested that sulphamide can also exist in an *aci*-form, thus, $SO_2{<}^{NH_2}_{NH_2} \rightleftharpoons$ $NH{:}SO{<}^{OH}_{NH_2}$, just as in the case of carbamide. The *sodium, lithium, potassium, barium,* and *calcium* salts are described as colourless, non-hygroscopic crystals, whilst the *cupritetrammine* and *cupriethylenediamine* salts were obtained as blue, crystalline solids.

Benzylidenesulphamide, $NH_2{\cdot}SO_2{\cdot}N{:}CHPh$, was obtained by the elimination of water from benzaldehyde and sulphamide by means of anhydrous copper sulphate. It forms needles, m. p. 135°, soluble in methyl alcohol, ethyl alcohol, and benzene. *Monochlorosulphamide*, prepared by the action of hypochlorous acid on sulphamide, melts at 66° with decomposition, and is easily soluble in water, alcohol, or chloroform. Details are given of an improved method of preparation of sulphamide from sulphuryl fluoride. H. H.

Protective Colloids. X. Saponin as Protective Colloid. III. Colloidal Selenium. A. GUTBIER and U. RHEIN (*Kolloid Z.*, 1923, **33**, 35—36; cf. A., 1921, ii, 538).—Colloidal solutions of selenium may be prepared by the cautious addition of a 1 : 1000 solution of hydrazine hydrate to solutions of selenious acid containing saponin with continuous stirring. During the formation, there is a continuous loss of selenium as a red precipitate due to the coagulation of the colloid in the foam produced. The sols

prepared are of various colours, vermilion, bright red, yellow, dark red, and bluish-red, the last-named being very unstable. Solutions, after dialysis, may be preserved for long periods, but have the property of settling into two layers which, however, may be readily made homogeneous again by simply shaking. The sols may be concentrated by freezing and warming, to both of which they are relatively stable, but the solid colloids are not entirely reversible and in many cases are quite irreversible. J. F. S.

Fixation of Atmospheric Nitrogen by the Cyanide Process. KIYOMATSU TERADA (*Rikwagaku Kenkyujo Ihô*, 1923, **2**, 234—242).—A mixture of 100 parts of sodium carbonate, 100 parts of potassium carbonate, 220 parts of charcoal, and 220 parts of ferric oxide was used as the catalyst. The reaction takes place at 600°; the yield of the cyanide is about 80% at 700°, and above 85% at 750°; the velocity of the passing nitrogen is 4·5—5 litres per minute, and the reaction is almost complete in sixty minutes. The catalyst was contained in an iron tube, which was scarcely acted on owing to the low temperature of reaction. K. K.

Synthesis of Ammonia from its Elements in the Low Voltage Arc. H. H. STORCH and A. R. OLSON (*J. Amer. Chem. Soc.*, 1923, **45**, 1605—1615).—The factors controlling the rate of formation of ammonia from nitrogen and hydrogen in the low voltage arc have been investigated. It is shown that the earlier work of Andersen (A., 1922, ii, 562), in which a wave type curve was obtained for the rate of reaction as a function of the accelerating voltage, is to be explained by the preliminary experiments described in the present paper. The curve is found to be due to a superposition of the curve described below and a "fatigue" factor in the mechanism used for absorbing the ammonia gas. The variation of the rate of reaction, at constant tube current, with the accelerating voltage is such as to give abrupt increases in the rate of reaction at specific voltages which are about four volts apart. The formation of ammonia in quantities sufficient to be detected by Nessler's reagent does not occur unless an arc is present. The magnitude of the rate at any given voltage, and at constant tube current, depends primarily on the diameter of the hot filament used as the source of electrons. An increased percentage of nitrogen in the gaseous mixture favours a higher rate of reaction. J. F. S.

Catalytic Oxidation of Ammonia by Air in Contact with Pure Palladium. E. DECARRIÈRE (*Compt. rend.*, 1923, **177**, 186—188).—Using an apparatus already described (this vol., ii, 155), the author has investigated the oxidation of ammonia by the above method. It is found that the yield of oxides of nitrogen is a function of the temperature of the catalyst and of the percentage of ammonia originally present, and also depends on the physical state of the metal.

E. E. T.

Catalysts for the Oxidation of Ammonia. I. KENKEI INABA (*Rikwagaku Kenkyujo Ihô*, 1923, **2**, 222—233).—A mixture of iron and bismuth was used as a catalyst for the oxidation of ammonia,

air being used as the source of oxygen. When the ratio of the oxides of iron and bismuth was 67 : 33, the yield was 85%; the temperature of the catalyst being 750—800°, thickness of the layer of the catalyst 0·5 cm., the current of gas contained 8% of ammonia and the velocity of the gas about 1 litre per minute. By adding thorium oxide to the catalyst, the yield was increased. If the content of oxygen in the gas is increased to 40%, the yield became 95%. The catalysts were prepared from the nitrates; oxides prepared by other methods gave a smaller yield. K. K.

The Formation of Nitric Acid in the Manufacture of Liquid Carbon Dioxide. L. HACKSPILL and A. CONDER (*Compt. rend.*, 1923, **176**, 1811—1813).—Under conditions which exclude the possibility of mechanical admixture, the potassium hydrogen carbonate which is formed as an intermediate product in the manufacture of carbon dioxide from coke contains a small quantity of potassium nitrite. This has its origin in the oxidation of the nitrogen content of the coke. The nitrous acid is partly liberated by the carbonic acid formed in the process and may be oxidised to nitric acid, which rapidly corrodes the plant in which the manufacture is carried out. H. J. E.

Crystal Structures of the Cubic Forms of Arsenious and Antimonious Oxides. RICHARD M. BOZORTH (*J. Amer. Chem. Soc.*, 1923, **45**, 1621—1627).—The crystal structures of arsenious and antimonious oxides have been determined by means of Laue photographs and *X*-ray photographs. These crystals may be regarded as composed of As_4O_6 and Sb_4O_6 molecules having a diamond arrangement, each molecule corresponding with one carbon atom. The arrangements are derived from the space group O_h^7. The sizes of the unit cubes containing eight molecules of As_4O_6 or Sb_4O_6 are 11·06 Å. for arsenious oxide and 11·14 Å. for antimonious oxide. The shortest distance between arsenic and oxygen atoms is 2·01 Å. and between antimony and oxygen atoms 2·22 Å. J. F. S.

Carbon. PELAYO POCH (*Anal. Fis. Quim.*, 1923, **21**, 291—304).—Carbon was prepared by decomposition of carbon monoxide passed through a porcelain tube in a combustion furnace with ferrosoferric oxide as catalyst, and also by the decomposition of cyanogen in an electric arc. *X*-Ray examination of the products obtained showed that the carbon from cyanogen was the more finely crystalline. Its heat of combustion was greater than that of carbon from carbon monoxide, but slightly less than that of Schering's "absorption carbon." The possibility of obtaining diamond from black carbon is discussed. G. W. R.

The Evaporation of Carbon. WERTENSTEIN and JEDRZEJEWSKI (*Compt. rend.*, 1923, **177**, 316—319).—The blackening of carbon filament lamps has been attributed to evaporation and also to disintegration of the filament. By studying the evaporation of carbon filaments in a vacuum, applying formulæ used by Fajans

A., 1920, ii, 469) and Langmuir (*Physikal. Z.*, 1913, **14**, 1273), it is shown that the above blackening is due to sublimation. The loss of carbon increases rapidly between 2,800° and 3,500° Abs., whereas if disintegration were the causal process no appreciable temperature coefficient would be observed. Also, the sublimate is distinctly crystalline. From the results obtained, the authors find the b. p. of carbon to be 5,100° Abs. (*i.e.*, a higher temperature than is reached in a carbon arc crater) and the atomic heat of sublimation, referred to the absolute zero, to be 216,000 cal. E. E. T.

Silicon Hydrides. XVI. The Higher Members of the Series. ALFRED STOCK, PAUL STIEBELER, and FRIEDRICH ZEIDLER (*Ber.*, 1923, **56**, [*B*], 1695—1705).—An investigation of the composition and properties of the less volatile silicon hydrides obtained by the action of acid on magnesium silicide. The liquid products were fractionally distilled in a vacuum and the fractions of the distillate collected at temperatures from −185° upwards. A yellow, amorphous, solid residue was obtained which, from its analysis and its behaviour towards bromine, appeared to be a polymeride of silicon monohydride, $[SiH]_x$. The following physical measurements were made. Silicopropane, Si_3H_8, d_4^0 0·743, m. p. −117·4°, b. p. 53°; silicobutane, Si_4H_{10}, d_4^0 0·825, m. p. about −90°, b. p. 109°. The higher members of the series are less stable to light and appear to decompose according to the scheme $Si_5H_{12} \longrightarrow 2[SiH]_x + Si_2H_6 + SiH_4$. This unsaturated hydride apparently cannot be obtained in a volatile form of low molecular weight. Whether obtained by the auto-decomposition of the silicoparaffins, by the action of the silent electric discharge on these compounds, by the action of acids on silicides, or by the action of sodium amalgam on silicoparaffins and their chlorides, it always appears in the solid, yellow, associated form, its composition varying between $[SiH]_x$ and $[SiH_{1\cdot 6}]_x$. H. H.

The Crystal Structure of Quartz. L. W. MCKEEHAN (*Physical Rev.*, 1923, **21**, 503—508).—It has been confirmed by the powder method of *X*-ray crystal analysis that the space lattice of quartz is hexagonal. An atomic arrangement consistent with the observed intensities of the lines requires the molecules to be obtuse-angled isosceles triangles, having an angle at the silicon atom centre of 115° 14′, and a distance between the silicon and oxygen atom centres of $1{\cdot}631 \times 10^{-8}$ cm., lying in the basal planes of each of three interpenetrating hexagonal space lattices. A. A. E.

Les Gaz Rares des Gaz Naturels. PROFESSOR CHARLES MOUREU, President of the Société Chimique de France (T., 1923, **123**, 1905—1947).—A lecture delivered before the Chemical Society on June 14th, 1923.

Equilibrium of Liquid and Gaseous Phases of Helium at Low Pressures. H. KAMERLINGH ONNES (*Rec. trav. chim.*, 1923, **42**, 535—538).—A discussion of the equilibrium between the liquid and gaseous phases of helium at very low pressures. It is shown that a maximum exists in the latent heat of vaporisation

of helium, as is predicted by the equation $L=Tdp/dT(v_s-v_l)$, but it is not so pronounced as calculations based on this equation indicate.

J. F. S.

Purification of Neon and a New Determination of the Critical Temperature of Neon. C. A. CROMMELIN (*Rec. trav. chim.*, 1923, **42**, 814—817).—A technique for the purification of neon is described which may be used for quantities up to 20 litres. The method consists in fractionation from a vessel originally at the temperature of boiling liquid hydrogen, after the removal of all gas which is not solidified at this temperature. With the pure material thus obtained, the author has redetermined the critical temperature and finds the value $-228·71°$ on the Kelvin scale.

J. F. S.

Preparation of the Alkali Metals. M. BUOU (*Bull. Soc. chim.*, 1923, [iv], **33**, 994—995).—Hackspill's method (A., 1911, ii, 602) is modified for students' use in that the vacuum is obtained by means of a water vacuum pump and drying tube. The reaction tube is heated at 350° until no more gas is evolved, when it is shut off from the pump and the temperature raised to 800°. The yield of metal is only slightly below that obtained by the original method.

H. H.

The Determination of the Degree of Hydration of Salts by a Radioactive Method. HENRY TERREY and VICTOR GEORGE JOLLY (T., 1923, **123**, 1979—1982).

The Causticisation of Potassium Carbonate. P. P. BUDNIKOV and J. K. SYRKIN (*Bull. Inst. Polytech. Ivanovo-Voznesensk*, 1923, **7**, 97—101).—The formation of potassium hydroxide from solutions of the carbonate and solid calcium oxide was studied at 20°. It was found that the reaction proceeded practically to completion (91 to 98%) if the initial concentration did not exceed $2N$; in more concentrated solutions there was a loss, due to the formation of the solid compound $K_2CO_3,CaCO_3$ (Barre, A., 1912, ii, 254); this loss is not observed if baryta or strontia is used instead of lime (Bodländer, A., 1905, ii, 634), the carbonates of these metals being unable to form such double salts. A curve is constructed to express the conditions governing the equilibrium of the reaction.

G. A. R. K.

Catalytic Decomposition of Sodium Hypochlorite by Cobalt Peroxide. OWEN RHYS HOWELL (*Proc. Roy. Soc.*, 1923, [*A*], **104**, 134—152).—The rate of decomposition of sodium hypochlorite by cobalt peroxide has been investigated at 25° and 50° under various conditions. It is shown that the rate of decomposition is directly proportional to the quantity of cobalt peroxide present. The rate of decomposition is accelerated by the presence of sodium salts; in the case of sodium chloride it is directly proportional to the square root of the concentration of sodium-ions present. This is explained by assuming the mechanism of the reaction to consist in the linking of hypochlorite-ions to the positive oxygen,

and sodium-ions to the negative oxygen of the peroxide, with subsequent immediate decomposition of the quadrivalent oxygen compound. In the presence of a fixed amount of hypochlorite, the rate is then proportional to the degree of adsorption of the sodium-ions. The rate is retarded by alkali, and the retardation is proportional to the adsorption of hydroxyl-ions. This is explained by the fact that hydroxyl-ions are attracted by the positive oxygen of the peroxide, yielding an inactive compound to the exclusion of hypochlorite-ions. The rate of the reaction has been measured at 25° and 50°, and the average temperature coefficient over this range is 2·37 and the Arrhenius activation coefficient E=16,574. The catalyst is not affected by any of the catalyst poisons, hydrogen sulphide, potassium cyanide, mercuric chloride, arsenious oxide. J. F. S.

The Allotropic Transformation of Ammonium Nitrate at 32°. P. MONDAIN MONVAL (*Compt. rend.*, 1923, **177**, 175—178; cf. Millican, Joseph, and Lowry, T., 1922, **121**, 959).—The solubility of ammonium nitrate has been determined carefully for the temperature range 26·7—39·2° (eleven readings), the transition-point being found to be 31·8° (240 g. of ammonium nitrate in 100 g. of water). The ratio of the tangents to the two halves of the curve (*ds*/*ds'*) was found to be 1·17, which (cf. Le Chatelier, *Compt. rend.*, 1900, **130**, 1606) should be equal to the ratio of the latent heats of solution for the two forms of the salt. The actual figure obtained for the second ratio (for method, cf. Mondain Monval, this vol., ii, 131) was 1·158 (*L*/*L'*), determinations being made at 28° and 36°. E. E. T.

Ammonium Dichromate. E. MOLES and F. GONZÁLEZ (*Anal. Fis. Quim.*, 1923, **21**, 204—212).—Data are given for the density, solubility, and heat of solution of ammonium dichromate. Tranquil decomposition takes place at about 225°, the oxidation of the ammonium to nitrogen being the most complete where the reaction takes place most rapidly. The black residue thereby obtained is shown to be chromium peroxide. G. W. R.

The Hydration of the Lithium-ion. J. BABOROVSKÝ and J. VELÍŠEK (*Chem. Listy*, 1923, **17**, 171—172; cf. A., 1921, ii, 573; 1922, ii, 816; this vol., ii, 288, 532).—Certain numerical data given in a preceding paper (A., 1922, ii, 816) are corrected. The degree of hydration of the kations of a solution of hydrochloric acid is found to be "four times less" than that of lithium kations, and cannot be accurately determined by gravimetric methods. An interferometer must be used. R. T.

Lithium-Ammonium. F. BENOIT (*Bull. Soc. chim.*, 1923, [iv], **33**, 908—917).—From a study of the isotherms obtained by the method of Biltz and Hüttig (A., 1921, ii, 201), it is shown that the lithium-ammonium poorest in ammonia is $Li,4NH_3$. This compound easily decomposes into lithamide, $LiNH_2$, hydrogen, and ammonia, and it is possibly this fact which led earlier investigators to describe compounds denoted by the erroneous

formulæ Li,NH_3 and $Li,3NH_3$. The analysis of the compound corresponds with the tetrammine formula, whilst molecular weight determinations point to the double formula $Li_2,8NH_3$. The heat of formation is given by the equation $2Li(solid)+8NH_3(gas)=Li_2,8NH_3(liquid)+8·67$ Cal. H. H.

Dispersoid Synthesis of Silver and Mercury by the Formaldehyde Method. P. P. von Weimarn (*Kolloid Z.*, 1923, **33**, 81—82).—Colloidal silver sols of great stability may be prepared by identically the same method as has been used for gold (see this vol., ii, 645). Mercury hydrosols are prepared by pouring 10 c.c. of a 0·04—0·075% solution of mercurous nitrate into 100 c.c. of a solution containing 90 c.c. of 0·2*N*-potassium hydroxide or potassium cyanide and 10 c.c. of 35% formaldehyde solution. Reduction takes place in either hot or cold solutions but is never complete, some mercurous oxide being formed. The mercury sol is yellow in colour and highly dispersed, but its colour changes rapidly to brown. The stability cannot be increased by boiling, for the mercury passes into the molecular disperse condition very rapidly. J. F. S.

General Colloid Chemistry. VII. Analysis and Constitution of Colloidal Silver. I. Paul Neureiter and Wo. Pauli (*Kolloid Z.*, 1923, **33**, 67—73; cf. this vol., ii, 329).—Measurements of the electrical conductivity of silver sols, prepared by the reduction of an ammoniacal solution of silver chloride by dilute hydrazine hydrate solution, have been carried out with the dialysed sol. The minimum precipitating values of potassium nitrate, silver nitrate, sulphuric acid, barium nitrate, and mercuric chloride have been found for the dialysed sol, and analyses of the coagulum and the filtrate made. The results indicate that unprotected colloidal silver has the composition and constitution represented by $[xAg\,.\,yAgCl\,.\,AgCl'_2]Ag\,.\,(NH_3)_2$. J. F. S.

Double Decomposition in the Absence of Solvents. I. The System Silver Nitrate–Mercuric Iodide. A. G. Bergman (*J. Russ. Phys. Chem. Soc.*, 1921, **53**, 181—191).—A fusion diagram is constructed for the system silver nitrate–mercuric iodide. Two *compounds*, $2AgNO_3,HgI_2$, yellowish-green crystals, m. p. 107°, and $AgNO_3,HgI_2$, m. p. 117—118°, are found to occur. The latter compound is dimorphous, its colour changing at 52° from canary-yellow to orange-yellow. It is interesting that no double decomposition occurs, as in the case of silver nitrate and potassium halides (Kablukov, A., 1907, ii, 865). This is probably due to the greater stability of the compounds in this case, and possibly also to the exothermic nature of the reaction which would be involved. R. T.

Symmetry of Calcium Thiosulphate Hexahydrate. W. T. Astbury (*Nature*, 1923, **112**, 53—54).—By the use of Bragg's ionisation spectrometer, it has been shown that the unit cell of calcium thiosulphate hexahydrate contains two molecules. The substance is therefore considered to be a member of the pinacoidal

class, rather than the unique example of the triclinic asymmetric class. A. A. E.

Studies on the Dolomite System. II. ALLAN ERNEST MITCHELL (T., 1923, **123**, 1887—1904).

System BaS_2O_6–$Na_2S_2O_6$–H_2O. W. C. DE BAAT (*Rec. trav. chim.*, 1923, **42**, 643—646).—The system sodium dithionate–barium dithionate–water has been investigated by means of solubility determinations at 30°, 20·1°, and 12°, and the results have been combined in an equilibrium diagram. It is shown that neither double salts nor mixed crystals are formed. J. F. S.

System Lead–Antimony. R. S. DEAN (*J. Amer. Chem. Soc.*, 1923, **45**, 1683—1688).—Investigation by means of differential heating curves and microscopic examination shows that antimony is soluble in solid lead up to between 2% and 3% of antimony at the eutectic temperature. The alloys containing up to 13% of antimony show a higher eutectic temperature on heating than on cooling. This is explained by hysteresis. A tentative equilibrium diagram has been constructed which assumes the existence of a compound, Pb_4Sb, containing 12·6% of antimony, which forms a eutectic with its solid solution in lead at 10% of antimony. The data are insufficient to fix these points accurately. The compound forms very slowly, and when the mixture is cooled it is not formed from the liquid, but from the solid eutectic between antimony and the solid solution. As a result of the reluctance of this compound to form, the system as it cools behaves as an antimony solid solution eutectic and hence freezes at 247°. When this is heated, the compound forms and the melting point is the eutectic point between the compound and the solid solution at 258°. J. F. S.

Thallic Sulphates and Thallic Selenates. JULIUS MEYER (*Rec. trav. chim.*, 1921, **42**, 614—619).—The solubility of thallic oxide, the basic sulphate, $Tl(OH)SO_4,2H_2O$, and the acid sulphate, $HTl(SO_4)_2,4H_2O$, has been determined in sulphuric acid of various concentrations from 10% to 90% at various temperatures and the stability diagram constructed. It is shown that no other thallic sulphate exists under the above-named conditions and that the other thallic sulphates described in the literature are mixtures the formation of which is due to the slowness of the change from one salt to another. The transition point of the two sulphates mentioned above lies at about 40°. The corresponding selenates have also been investigated, and are found to be very similar to the sulphates; the main point of difference between them is that the transition point lies at 45°. J. F. S.

Separation of Isotopes. Application of Systematic Fractionation to Mercury in a High Speed Evaporation-Diffusion Apparatus. ROBERT S. MULLIKEN (*J. Amer. Chem. Soc.*, 1923, **45**, 1592—1604; cf. this vol., ii, 31).—An apparatus is described for the rapid partial separation of mercury into its isotopes by a combined process of distillation and molecular diffusion at low

pressure, the latter process being the major factor in the separation. The diffusion membrane in each unit consists of a tube of filter-paper a metre long, this material being selected primarily because of its thinness. The operation of the apparatus is carried on as a systematic fractionation, in which six units are used independently. Preliminary operation of the apparatus has given a separation of 0·102 unit of atomic weight between extreme fractions of 22 c.c. A separation of 0·3 unit with 50 c.c. fractions should be obtainable in a year of steady work. The method by which the new value, 0·0063, for the separation coefficient of mercury was obtained is described in connexion with the preliminary studies on the design of the apparatus. Systematic fractionation requires the maintenance of a permanent stock of intermediate fractions, of some minimum size, Q_0, in order to extend the range of a separation. A thorough study of the course of systematic fractionation has yielded valuable results which are applicable to all methods of separation by diffusion or in an analogous manner. The simple and systematic method of fractionation in which a cut of two is made in each individual operation is probably the most rapid for practical operation. The time required for the production of any fraction after the necessary preliminary or intermediate fractions have been produced is given by the formula $t=C(\Delta M)^2Q_0/DE^2B^2$, where E is the efficiency, B the separation coefficient, D the rate of production of the light fraction, and C a constant. This serves to establish a criterion for the value (V) of any fraction, which may be defined as $V=(\Delta M)^2Q$. This criterion is applied to the calculation of loss of value by mixing and other causes. The time required for the production of any extreme fraction, taking into account the total time used in building up the intermediates, is given by $t=C'(\Delta M)^3Q_0/DE^3B^3$. A consideration of this equation shows the difficulty of obtaining large values of ΔM, especially if B is low. It also shows the relative importance of Q_0, D, and E, and this relation, somewhat modified by other practical considerations, was used in the design and is also used in the operation of the present apparatus. The optimum speed of operation is shown to be that for which $E^{3.5}D$ or E^4D is a maximum. The equation above can also be used as a basis for a criterion of value for extreme fractions, namely $V'=(\Delta M)^3Q$. The approximate proportionality of the time required for a given separation to the cube of the degree of separation shows that whilst considerable separations can be effected by systematic fractionation, nothing approaching complete separation can be expected by methods of the diffusion type, unless in the most favourable cases and by factory scale operation. It is further, the opinion of the author that there seems to be little prospect that any other method or methods yet proposed will prove greatly superior to those of evaporation and molecular diffusion, although the centrifugal method may prove useful especially for elements of higher atomic weight. For any particular element, the most favourable method depends greatly on the nature of the substance.

J. F. S.

Surface Tension of Mercury in the Presence of Oxygen. T. BATUECAS (*Anal. Fis. Quim.*, 1923, **21**, 259—264; cf. Palacios and Lasala, this vol., ii, 166).—The surface tension of freshly distilled mercury decreases in air or in oxygen containing traces of ozone. This is attributed to condensation on the surface and not to chemical reaction between ozone and mercury. G. W. R.

The Replacement of the Metals of the Second Odd Group of the Periodic System from their Salt Solutions by Means of Hydrogen at High Temperatures and Pressures. W. IPATIEV and A. STARYNKEVITSCH (*Ber.*, 1923, **56**, [*B*], 1663—1667).—A study of the conditions under which hydrogen will react with aqueous solutions of the salts of mercury, zinc, cadmium, and magnesium. Hydrogen at 100 atm. for thirteen hours at 160° reduces a solution of mercurous nitrate to metallic mercury and a salt which may have the formula $2Hg_2O,N_2O_5$. When heated at 225°, reduction to metallic mercury is complete. Mercuric nitrate is similarly reduced to the mercurous salt at 170—180°, and to metallic mercury at 240—250°. Cadmium nitrate at 110 atm. and 180° is not attacked, but at 135 atm. and 220° it yields a hitherto unknown salt of the composition $Cd(NO_3)_2,7CdO$. At 270° and 220 atmospheres, the nitrate is further reduced to crystalline, metallic cadmium. Cadmium sulphate at 250 atm. and 260—290° is reduced to the yellow, crystalline sulphide and traces of metallic cadmium. Zinc nitrate is similarly reduced to the oxide and the metal, whilst the sulphate under corresponding conditions yields the sulphide and the metal. Magnesium nitrate was reduced to the hydroxide, but not to the metal, whilst the sulphate gave, first, the sulphide and, later, the hydroxide. It is noteworthy that the solid products of these reactions were almost invariably deposited in a crystalline form.

The reduction of carbonates to formates under similar conditions was also studied. Potassium hydrogen carbonate was reduced to the formate in 11% yield by heating for four hours with hydrogen under 380 atm. at 350°. H. H.

The Precipitation of Metals by Hydrogen Sulphide. G. McPHAIL SMITH (*Science*, 1923, **57**, 447—449; cf. Neuhausen, this vol., ii, 396).—On treatment of an aqueous solution of mercuric perchlorate (prepared by dissolving mercuric oxide in excess of perchloric acid, evaporating to small volume, and crystallising) with a solution of hydrogen sulphide, precipitation does not at first occur, but there is obtained a brown, opalescent solution which gives a white precipitate with hydrochloric, nitric, or sulphuric acid. The solution, which evidently contains a complex salt, on keeping deposits white crystals of the compound $Hg(ClO_4)_2,2HgS$. A. A. E.

Phototropic Compounds of Mercury. M. L. DEY (*Nature*, 1923, **112**, 240; cf. Venkataramaiah and Rao, this vol., i, 764).—Phototropy is exhibited to a greater or less extent by complex salts of the formula HgS,HgX_2 or $2HgS,HgX_2$, where X is a halogen or univalent acid radicle, including thiocyanate. A. A. E.

Positive Ray Analysis of Copper. A. J. DEMPSTER (*Nature*, 1923, **112**, 7; cf. Aston, this vol., ii, 596).—By the use of a molybdenum furnace, three isotopes of copper have been observed separated by two units in atomic weight, and having relative intensities 1·4 : 1 : 1. Failing direct comparison, a consideration of the chemical atomic weight of copper indicates the masses of the isotopes to be 62, 64, and 66, respectively. The existence of two isotopes of molybdenum, giving a mean atomic weight of 85·51, was confirmed. A. A. E.

The Melting-point and Equilibrium Diagram of the Copper-Tin Alloys. O. BAUER and O. VOLLENBRUCK (*Z. Metallk.*, 1923, **15**, 119—125, 191—195).—Copper retains a maximum of 13·9% of tin in solid solution, but tin can retain only traces of copper. The compound Cu_3Sn exists in two modifications; the α-form is stable up to 676°, above which the β-form is the stable modification and melts unchanged at 720°. The existence of the compound Cu_4Sn has been definitely proved, and a new compound, Cu_6Sn_5, has been found in and isolated from alloys containing more than 60% of tin. It is stable below the eutectic point at 225° in all alloys containing more than 61% of tin. [Cf. *J.S.C.I.*, 1923, **42**, 227A.] A. P. R.

Binary Systems of Salts with Components Capable of Sublimation. ERNST JÄNECKE (*Rec. trav. chim.*, 1923, 42, 740—744).—A discussion of binary systems of two salts, one of which may be sublimed. The systems described are: cuprous chloride–mercurous chloride, in which the eutectic lies at 330° with 65% of mercurous chloride; silver chloride–mercurous chloride, which has a eutectic at 250° with 55% of mercurous chloride; silver chloride–ammonium chloride, which has a eutectic at 245° with 80% of ammonium chloride; mercurous chloride–ammonium chloride, in which the mass is completely melted at a composition between 17 and 25% of mercurous chloride, and in which the eutectic lies at 135° with 79% of mercurous chloride; mercuric chloride–ammonium chloride, which forms two compounds, $HgCl_2,NH_4Cl$ and $HgCl_2,4NH_4Cl$. The first compound has m. p. 204° and b. p. 350°, and forms clear, lustrous crystals with a weak double refraction. The second compound, m. p. 244°, decomposes when heated into ammonium chloride and a liquid containing 70% of mercuric chloride. J. F. S.

Formation of Sulphide, Selenide, and Telluride of Copper. FELICE GARELLI (*Rec. trav. chim.*, 1923, **42**, 818—820).—A discussion of the formation of sulphide, selenide, and telluride of copper when the respective non-metals, wrapped with copper wire, are placed in a solution of a copper salt. With cold solutions, cupric derivatives are formed, but with boiling solutions, the cuprous compounds are formed. J. F. S.

The Crystal Structure of Various Heusler Alloys, by the Use of X-Rays. J. F. T. YOUNG (*Phil. Mag.*, 1923, [vi], 46, 291—305).—By the method of *X*-ray analysis, the author has

determined that aluminium and copper crystallise in a face-centred cubic system of lattice constant 4·05 Å. and 3·60 Å., respectively. In the case of two Heusler alloys of definite composition, the magnetic properties of which were studied by McLennan (*Physical Rev.*, 1907), it is shown that these occur in two crystal forms, *viz.*, a face-centred cubic crystal of constant 3·70 Å., and a combination of this with a body-centred cubic crystal of lattice constant 2·98 Å. It is tentatively suggested that the alloys are solid solutions of manganese–aluminium alloy in copper, and the author considers that the magnetic effects exhibited by the alloys are ultimately associated with the valency electrons, and not with the molecule or atom or any complex group of these. J. S. G. T.

The Ternary System: Aluminium–Zinc–Tin. E. CREPAZ (*Giorn. Chim. Ind. Appl.*, 1923, **5**, 115—285).—The experiments performed confirm the equilibrium diagram for zinc–tin alloys as obtained by Lorenz and Plumbridge (A., 1913, ii, 1056). It was found that the relative variation of the potential of the cell $Sn_xZn_{(1-x)}|NZnSO_4|EN$ with mercurous chloride is equal to that of the cell investigated by Herschkowitsch, $Zn|NSO_4|Sn_xZn_{(1-x)}$.

The equilibrium diagram given by Gwyer for aluminium–tin alloys was also confirmed. The regular variation of the hardness diagram shows the improbability of the existence of solid compounds or solutions.

The superficial treatment has a strong influence on the potential of aluminium. The cell $Al|N/10KAl(SO_4)_2|EN$ with mercurous chloride gives a maximum value of 1·1 volts.

It was found that the potential of aluminium–zinc alloys is independent of concentration, higher than that of aluminium, and practically constant in the whole interval of concentration. For the cell $Al_xSn_{(1-x)}|N/10KAl(SO_4)_2|EN$ with mercurous chloride 1·4 volts was found to be a mean constant value.

Hanson and Gayler's equilibrium diagram was confirmed, however, with formation of a solid solution instead of the compound Al_2Zn_3.

The study of the ternary alloy aluminium–zinc–tin together with the micrographic investigation thereof, shows that the eutectoid is practically independent of aluminium, and may be identified with the eutectoid of the binary alloy zinc–tin. The decomposition of the solid solution, β, is favoured by the presence of tin.

The mechanical properties of quenched alloys containing β vary with time. Their hardness seems to reach a definite value after four days. E. M. V.

Equilibrium Studies in the Quaternary System Aluminium–Magnesium–Silicon–Zinc. W. SANDER and K. L. MEISSNER (*Z. Metallk.*, 1923, **15**, 180—183).—The equilibrium diagrams of the four tertiary systems are briefly considered, and from these the quaternary diagram, in which each of these four systems is reproduced on a side of a regular tetrahedron, is built up. No tertiary or quaternary compounds are formed, although five binary compounds, Al_3Mg_4, Al_3Mg_2, AlZn, $MgZn_2$ and Mg_2Si, are

known; consequently the whole system may be divided into seven separate quaternary systems. [Cf. *J.S.C.I.*, 1923, **42**, 892A.]

A. R. P.

[Method for] The Sublimation of Aluminium Chloride. EINAR BIILMANN (*Bull. Soc. chim.*, 1923, [iv], **33**, 995—996).—Freshly sublimed aluminium chloride is very necessary for Friedel and Crafts' reactions, and may be obtained in about 40 g. quantities by the following method. The lower part of a test-tube ($1\frac{1}{2}$ inches × 7 inches) is surrounded with a jacket of wire gauze and is supported in an inclined position. The upper portion is cooled by means of a stream of water and a cotton wick. By the application of heat, the chloride may be made to sublime from the lower to the upper part of the tube.

H. H.

Separation of Gallium from Commercial Aluminium. R. LLORD Y GAMBOA (*Anal. Fis. Quim.*, 1923, **21**, 280—284).—The presence of gallium has been verified spectroscopically in samples of bauxite and aluminium. A method is described for the separation of gallium. [See, further, *J.S.C.I.*, 1923, **42**, 780A.] G. W. R.

Permanganates. III. E. MOLES and M. CRESPI (*Anal. Fis Quim.*, 1923, **21**, 305—315; cf. this vol., ii, 161, 565).—A description of the preparation and properties of the permanganates of silver, copper, glucinum, magnesium, zinc, and cadmium. Those which decompose at high temperatures give a residue stable up to 450°, consisting of the manganite and a solid solution of the manganate and manganese peroxide. Those decomposing at lower temperatures yield below 450° all the oxygen corresponding with the decomposition of the manganate and manganese peroxide. The temperature of decomposition of the permanganates is shown to be a periodic function of the atomic number of the metals. G. W. R.

Oxides of Iron. JOHN B. FERGUSON (*J. Washington Acad. Sci.*, 1923, **13**, 275—281).—The system hydrogen–water vapour–iron–ferrous oxide has been investigated. It is shown that the iron phase does not contain appreciable quantities of oxygen. The transition temperature of the ferrous oxide phase appears to be lowered by solution of the magnetic oxide in it. The quadruple point lies below 577°. A value, which is slightly less than 0·54, and certainly less than 0·57, has been obtained for the equilibrium constant, $K = H_2O/H_2$, at 750° by the stream method. This agrees with the value obtained by interpolation from the results of Chaudron (A., 1914, ii, 721; 1921, ii, 178, 584), and furnishes a confirmation of the latter.

J. F. S.

Iron and the Lower Oxides of Iron. JOHN BRIGHT FERGUSON (*Canad. Chem. and Met.*, 1923, **7**, 175—176).—No change takes place if pure iron is heated in a mixture of hydrogen and water vapour at temperatures above 750°, and slightly oxidised specimens of iron were completely reduced after this treatment, thus showing that iron forms no oxide lower than ferrous oxide. Ferrous oxide appears to be stable above 526°; below that temperature it decom-

poses into iron and ferrosoferric oxide, thus, $4FeO \rightleftharpoons Fe+Fe_3O_4$, provided the temperature is not too low. The reaction is strictly reversible, the mixture being quantitatively reconverted into ferrous oxide above 607°, although the reaction starts at 577°. Admixture of ferric oxide with ferrous oxide lowers the transition temperature. Oxidation of iron at 750° begins to take place with a gas mixture having a ratio of water vapour to hydrogen of slightly less than 0·54. A. R. P.

Preparation of Easily Filtrable Iron Hydroxide by Precipitation with Thiosulphate and Iodate. FRIEDRICH L. HAHN and MARIA HERTRICH (*Ber.*, 1923, **56**, [*B*], 1729—1732).—A method of precipitation of bi- or ter-valent iron is described which is simple, rapid, and cheap; it gives a heavy, powdery precipitate, easily washed and filtered, which contains no basic salt even when moist, and gives the theoretical quantity of iron oxide on ignition. The reactions involved are: $2Fe^{\cdot\cdot\cdot}+2S_2O_3''=2Fe^{\cdot\cdot}+S_4O_6''$, $2Fe^{\cdot\cdot}+6H_2O+IO_3'+4S_2O_3''=2Fe(OH)_3+I'+2S_4O_6''$. A ferric salt is neutralised and then warmed with thiosulphate solution until practically colourless. It is then warmed with twice the theoretical quantity of thiosulphate and a slight excess of iodate calculated on the second of the above equations. Ammonium chloride should be added before the iodate. The volume of solution from which precipitation occurs should be about 400 c.c. for every 0·2 g. Fe_2O_3. It is sufficient to warm the solutions on the water-bath, but the precipitate should be ignited at the blow-pipe. A ferrous salt is naturally not reduced, but is precipitated straightaway from a neutral or slightly acid solution. H. H.

Iron and Copper Oxides. RUDOLF RUER and MINOBU NAKAMOTO (*Rec. trav. chim.*, 1923, **42**, 675—682).—The region of stability and the pressure of oxygen in equilibrium with ferric oxide and cupric oxide have been investigated. In the case of ferric oxide, it is shown that heating this substance in a current of pure dry nitrogen causes no loss of weight at temperatures up to 1125°; at 1200°, the oxide loses 3·28% of its weight, and above this temperature oxygen is lost continuously up to 1550°, when the substance melts. A repetition of the experiment shows that oxygen is lost very slowly at 1150°, and this is the lowest temperature at which a loss of oxygen occurs. The loss of oxygen at 1150° continues until the compound Fe_3O_4 is formed, which contains about 2% of ferric oxide dissolved in it. At 1550°, the solid is the magnetic oxide containing 4% of ferrous oxide in solid solution. Further experiments, in which ferric oxide was heated in air and oxygen, respectively, are described, which show that at 1470° ferric oxide loses oxygen when heated in this gas at 1 atm. pressure, but takes up the amount lost at 1440°. From this it follows that the dissociation pressure of ferric oxide is 1 atm. at 1455°. The dissociation pressure at 1150° is scarcely measurable, and at 1383° it is 0·20 atm. Similar experiments with cupric oxide show that at 775° this substances loses oxygen in a stream of nitrogen and passes into cuprous oxide; the rate of loss is much more rapid at 800°,

but at both temperatures the change to cuprous oxide may be completed without the formation of any intermediate compound. Cuprous oxide is quite stable in a current of nitrogen at temperatures up to 1222°, when it melts. Cupric oxide has a dissociation pressure of 1 atm. at 1105°, and at 1109° the mixture of cuprous and cupric oxides melts. The dissociation pressure at 1031° is 0·20 atm. J. F. S.

Solubility. VIII. The Solubility of Cobaltammines. FRITZ EPHRAIM (*Ber.*, 1923, **56**, [*B*], 1530—1542).—The theory is developed that solubility depends on solvate formation between solute and solvent. Aqueous solutions are considered, and it is maintained that there are three factors influencing the possibility of solvate formation: (*a*) relative size of anion and kation, disparity in size favouring solubility; (*b*) the heat of hydration of the ions, inequality again favouring solubility; (*c*) the effect of steric hindrance. The solubilities of many cobaltammine salts are given and several regularities are pointed out. The polar character of the mechanism of solvate formation is supported by the fact that, whilst salts with tervalent kations, *e.g.*, $[Co(NH_3)_6]^{\cdot\cdot\cdot}$, bivalent kations, *e.g.*, $[Co(NH_3)_5Cl]^{\cdot\cdot}$, and univalent kations, *e.g.*,

$$[Co(NH_3)_4(NO_2)_2]^{\cdot},$$

are soluble, neutral molecules of the type $[Co(NH_3)_3(NO_2)_3]$ are practically insoluble. The last are also non-electrolytes. The following new compounds are mentioned. *Hexamminecobaltifluosilicate*; *monoaquopentamminecobaltiperchlorate*, the *naphthalene-β-sulphonate*, *picrate*, and *iodide*; *diaquotetramminecobaltinitrate*, the *picrate* and *naphthalene-β-sulphonate*; *chloropentamminecobaltiperchlorate*, *picrate*, *naphthalene-β-sulphonate*, *thiosulphate*, and *oxalate*; *bromopentamminecobalti-iodide*, the *perchlorate*, *chlorate*, *thiosulphate*, *picrate*, and *naphthalene-β-sulphonate*; *iodopentamminecobaltichlorate*; *nitropentamminecobalti-iodide*, the *perchlorate*, *picrate*, and *naphthalene-β-sulphonate*; *nitratopentamminecobalti-iodide*, the *chlorate*, *perchlorate*, *fluosilicate*, *picrate*, and *naphthalene-β-sulphonate*; cis-*dinitrotetramminecobaltibromide*, the *chlorate*, *perchlorate*, *fluosilicate*, and *picrate*; trans-*dinitrotetramminecobaltichlorate*, the *perchlorate*, *fluosilicate*, *oxalate*, and *picrate*. H. H.

Crystal Structure of Natural and Synthetic Oxides of Uranium, Thorium, and Cerium. V. M. GOLDSCHMIDT and L. THOMASSEN (*Videnskapsselskapets Skrifter. Mat. Naturv. Klasse*, 1923, 5—48; from *Chem. Zentr.*, 1923, i, 1149—1150).—Pitchblende, bröggerite, cleveite, thorianite, and the oxides of uranium, thorium, and cerium were examined by the Debye-Scherrer and Laue methods. The dioxides (uranous oxide, cerium dioxide, and thorium dioxide) are isomorphous. The metallic atoms are arranged in a regular face-centred lattice, and the oxygen atoms probably in a lattice of the calcium fluoride type. The edges are, for uranous oxide, 5·47 Å., for thorium dioxide, 5·61 Å., and for cerium dioxide, 5·41 Å. The structure of uranoso-uranic oxide (U_3O_8) is irregular. Uranic oxide was only obtained in an amorphous form. The minerals all show crystal structure, the edges being for thorianite, 5·57 Å.;

for bröggerite, 5·47 Å., and for cleveite, 5·47 Å. They correspond with isomorphous mixtures of the three oxides and also of lead peroxide. The crystalline substance in thorianite and bröggerite has a uniform arrangement with a distortion of the single points as if the crystal were composed of sub-parallel planes. Cleveite yields uranosouranic oxide on ignition. Bröggerite, after ignition, shows the uranous oxide structure. The crystal substance in pitchblende is present in a finely divided state (10^{-4} to 10^{-7} cm.). The uranium atoms form face-centred cubes with edges 5·42—5·45 Å. It is supposed that, as the ground lattice of these minerals is uranous oxide, the excess of oxygen corresponding with uranic oxide is present in solid solution. This case is analogous to the occurrence of yttrium fluoride in calcium fluoride. Bröggerite in which uranium is partly transformed to lead retains the original lattice arrangement. G. W. R.

Should the Element of the Atomic Number 72 be called Celtium or Hafnium? G. Urbain (*Chemistry and Industry*, 1923, **42**, 764—769).—The author reviews briefly the literature dealing with the element of atomic number 72, and advances a claim to its discovery prior to the work of Coster and von Hevesy. A bibliography of the subject is given. J. S. G. T.

Hafnium and Celtium. Harold S. King (*Nature*, 1923, **112**, 9).—Priority is claimed for the statement that the chemical properties of celtium, as described by Urbain, do not agree with theoretical considerations of atomic structure. A. A. E.

The Discovery of Hafnium and the Present Position of our Knowledge of this Element. Georg von Hevesy (*Ber.*, 1923, **56**, [*B*], 1503—1516).—A summary of the work leading up to the discovery of hafnium and an account of its physical and chemical properties as far as at present known. H. H.

Dispersoid Synthesis of Gold. I. P. P. von Weimarn (*Kolloid. Z.*, 1923, **33**, 74—81).—Making use of ordinary distilled water and commercial reagents, bright red gold sols are prepared by adding 10 c.c. of a 0·1% solution of chloroauric acid ($HAuCl_4,4H_2O$) to 500 c.c. of water and, with vigorous stirring, 10 c.c. of a solution containing 12 g. of potassium hydroxide and 100 c.c. of 35% formaldehyde solution per litre. The reduction is instantaneous, but the sol produced is not very stable; usually after forty-eight hours it has completely coagulated. If, however, the reaction is carried out at the boiling point and the sol boiled gently for some time, it is found that the stability increases with the time during which it has been boiled. Thus after five minutes' boiling the sol coagulates in forty-eight hours, after sixty minutes' boiling it is stable for several months. Similar sols of similar properties may also be obtained by substituting an approximately 0·2N-solution of potassium carbonate for the potassium hydroxide. J. F. S.

Mineralogical Chemistry.

Fumaroles of the Katmai Region, Alaska. E. T. ALLEN and E. G. ZIES (*Contrib. Tech. Papers, National Geogr. Soc., Washington*, 1923, *Katmai Ser.*, No. 2, 75—155).—An illustrated account is given of the fumaroles in the "Valley of Ten Thousand Smokes," and the methods of recording the temperatures (50° to 650°) and collecting the gases are described. Steam forms 98·65 to 99·85 vol.% of the gases, the remainder being hydrogen chloride, carbon dioxide, hydrogen sulphide, nitrogen, hydrogen fluoride, and sometimes methane, with minor quantities of oxygen, carbon monoxide, argon, and ammonia. The water is probably of surface origin, and the nitrogen and argon are from the atmosphere. Incrustations include ammonium chloride, sulphur, iron salts, and rarely arsenic sulphide. L. J. S.

Transparent Preparations of Coal for Microscopical Investigations. J. LOMAX and J. R. LOMAX (*Lancs. Cheshire Coal Res. Assoc. Bull.*, 1923, No. 14).—A discussion of various methods for the preparation of transparent sections of coal and a detailed description of one found very satisfactory in practice. T. S. W.

Vauxite and Paravauxite, Two New Minerals from Bolivia. SAMUEL G. GORDON (*Proc. Acad. Nat. Sci. Philadelphia*, 1923, 75, 261—270).—These occur on wavellite in brecciated tin-veins in rhyolite at Llallagua, Oruro. Vauxite occurs as radiating aggregates of sky-blue, triclinic crystals with $a:b:c=1·1510:1:1·2624$, $\alpha=98°32'$, $\beta=102°\ 14'$, $\gamma=110°\ 14'$; d 2·375, H. 3½; refractive indices α 1·551, β 1·555, γ 1·562, optically positive. Paravauxite forms colourless, triclinic crystals of prismatic habit with good b (010) cleavage; $a:b:c=0·5058:1:0·6882$, $\alpha=97°\ 42'$, $\beta=110°\ 22'$, $\gamma=100°\ 56'$; d 2·291, H. 3; refractive indices α 1·554, β 1·558, γ 1·573, optically positive. Analyses by J. E. WHITFIELD gave I for vauxite and II for paravauxite.

	FeO.	MnO.	Al_2O_3.	P_2O_5.	H_2O at 104°.	H_2O above 104°.	Total.
I.	19·34	0·18	14·89	31·33	3·68	30·24	99·60
II.	15·47	—	17·89	29·80	16·40	20·34	99·90

The minerals are readily soluble in hydrochloric acid. The water content of the paravauxite varies considerably with the humidity of the atmosphere. Formulæ:

Vauxite: $4FeO,2Al_2O_3,3P_2O_5,24H_2O+3H_2O$.

Paravauxite: $5FeO,4Al_2O_3,5P_2O_5,26H_2O+21H_2O$.

L. J. S.

Electronic Structures of the Spinels. MAURICE L. HUGGINS (*Physical Rev.*, 1923, **21**, 509—516).—In the cases of crystals of the formulæ $ZnAl_2O_4$, $ZnCr_2O_4$, $ZnFe_2O_4$, $MgAl_2O_4$, $MgCr_2O_4$, $MnAl_2O_4$, $MnCr_2O_4$, $CdCr_2O_4$, and $FeFe_2O_4$, the distances between adjacent atomic centres have been calculated from the densities, and the

positions of the oxygen centres determined. The densities of the compounds $MgFe_2O_4$ and $MnFe_2O_4$ are calculated to be 4·47 and 4·90 g./cm.^{3}, respectively. When the oxygen radius (the distance from the atomic centre to the valency electron-pair) is assumed to be 0·65 Å., atomic radii may be computed as follows: Zn^{+2}, 1·31 Å.; Fe^{+2}, 1·27—1·30; Mg^{+2}, 1·29; Mn^{+2}, 1·39; Cd^{+2}, 1·51; Fe^{+3}, 1·38; Al^{+3}, 1·26; Cr^{+3}, 1·35. It is considered that the empirical formula $R''R'''_2O_4$ is the only one which correctly represents the structure of the spinels in the crystalline state. A partial explanation of the cause of ferromagnetism may possibly be found in the suggestion that it arises from a concentration of electron triplets in the same end of each atomic kernel. A. A. E.

The Chemical Formula of Uraninite. ALFRED SCHOEP (*Bull. Soc. chim. Belg.*, 1923, **32**, 274—281).—The author has analysed specimens of Katanga pitchblende, estimating total uranium as U_3O_8 and UO_2 in presence of UO_3 by Hillebrand's method of heating the mineral in a sealed tube with dilute sulphuric acid in an atmosphere of carbon dioxide, and volumetric estimation of the dioxide with potassium permanganate. The results lead to the conclusion that the purified mineral (*i.e.*, uraninite) has the formula $(UO_2)_3(UO_3)_2$ (cf. Blomstrand, A., 1884, 1102). This is discussed in comparison with results obtained by other workers for pitchblende from Katanga and other sources, and also for thorianite, and reasons are given for regarding the UO_3 as an oxidation product of the UO_2 of which the original mineral consisted. Thus the author maintains that the formula of uraninite is UO_2 as that of thorianite is ThO_2, the two minerals being isomorphous and analogous in chemical composition. The percentage of the dioxide is greater in fresh specimens of the mineral; some consist of ThO_2,UO_3 in which all the uranium compound has undergone oxidation. Thorianite contains various proportions of UO_2 and isomorphous mixtures of the two dioxides may be prepared artificially. H. J. E.

Bavalite from Bas-Vallon, Brittany. J. ORCEL (*Compt. rend.*, 1923, **177**, 271—273).—Bavalite is an oolitic iron-ore consisting of a mixture of chlorite and magnetite: the name is restricted to the chloritic constituent. The pure sample analysed has *d* 3·20; it is finely scaly, and is optically negative with small axial angle. Analysis gave:

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	CaO.	Alkalis.	H_2O.	Total.
21·71	0·08	21·35	0·82	43·01	0·05	2·33	0·16	0·35	10·21	100·07

This corresponds with $2SiO_2,Al_2O_3,3FeO,3H_2O$, or a ferrous salt of the acid $Al_2Si_2O(OH)_{12}$. Of the water 0·11% is lost at 107°, 9·03% at 485°, and 1·07% at 735°. The composition is near that of chamosite. L. J. S.

Hodgkinsonite, Datolite, and Calciothomsonite from Franklin, New Jersey. SAMUEL G. GORDON (*Proc. Acad. Nat. Sci. Philadelphia*, 1923, **75**, 271—274).—Crystallographic descrip-

tions are given of hodgkinsonite and datolite. The calciothomsonite is colourless and radiating with d 2·405, and refractive indices for yellow mercury light $\alpha=1·530$, $\beta=1·532$, $\gamma=1·542$. Analysis by J. E. WHITFIELD shows the mineral to be thomsonite with $CaO:Na_2O=5:1$.

SiO_2.	Al_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	H_2O at 100°.	$H_2O>100°$.	Total.
36·44	30·34	15·94	trace	3·50	0·18	0·26	13·26	99·92

L. J. S.

Analytical Chemistry.

X-Ray Spectroscopy as a Means of Qualitative and Quantitative Chemical Analysis. D. COSTER (*Chem. News*, 1923, **127**, 65—70).—A useful summary of present knowledge.

Screw Modification of the Mohr Pinch Clamp. WILLIAM M. CRAIG (*J. Amer. Chem. Soc.*, 1923, **45**, 1723).—A modification of the Mohr pinch clamp is described which allows a dropwise delivery from a burette. The modification consists in removing one of the finger plates from the ordinary pinch clamp and soldering it through a hole to a piece of brass plate 3 mm. thick, 10 mm. wide, and 20 mm. long. This plate lies in such a position that its length is above the straight arms of the clamp. A hole is bored through the brass plate, tapped, and fitted with a suitable screw, which is left in such a position that it prevents the clamp being opened more than enough to allow the liquid to pass more rapidly than dropwise when the clamp is opened. The screw may be adjusted to allow any desired rate of flow from the burette.

J. F. S.

The Electrometric Titration of Acids and Bases with the Antimony Indicator Electrode. ALFRED UHL and WILHELM KESTRANEK (*Monatsh.*, 1923, **44**, 29—34).—The hydrogen and mercury–mercuric oxide electrodes possess certain disadvantages in electrometric titrations, the copper electrode is not satisfactory, and a silver–silver oxide electrode is useful only in absence of chloride-ions. A suitable metal for the electrode must be insoluble in dilute acids, must respond accurately to hydroxyl-ion concentration, and its oxide must possess a very small solubility-product. A metal giving salts which are hydrolytically dissociated to a high degree by water, and giving an amphoteric hydroxide, should provide an excellent electrode. Antimony satisfies these requirements.

Good results were obtained initially, using an antimony electrode in presence of antimony oxide, but it was afterwards found that antimony, after being cast, contains sufficient oxide for the purpose of providing an efficient electrode. Decinormal solutions of sodium hydroxide were titrated satisfactorily against similar solutions of hydrochloric acid (at 15°, at 50°, and also in presence of large

quantities of ammonium nitrate) and acetic acid (in presence or absence of potassium chloride). Tartaric acid gave only slightly less good results. Constant potential (after each addition of titrating liquid) was attained within thirty seconds, but it is not necessary to wait for this constancy, owing to the sensitiveness of the electrode.

A simple apparatus in which the side tube of a calomel electrode is replaced by an H-tube, the latter being in contact with the solution to be titrated, is described. E. E. T.

Limits of Hydrogen-ion Concentration as Determined by Electrometric Titrations in Water Solutions of Carbon Dioxide, Calcium Sulphate, and Calcium Carbonate. J. W. SHIPLEY and IVAN R. MCHAFFIE (*J. Soc. Chem. Ind.*, 1923, **42**, 311—319T).—A method for performing an electrometric titration with carbon dioxide gas is described. The range of hydrogen-ion concentration for mixtures of calcium carbonate and carbon dioxide (up to a partial pressure of 1 atm.) in aqueous solution has been determined experimentally by means of the hydrogen electrode. The range of hydrogen-ion concentration in solutions containing calcium carbonate, calcium sulphate, and carbon dioxide has been determined experimentally. A strong buffer solution is produced at a hydrogen-ion concentration of $7{\cdot}77\times10^{-6}$ or p_H 5·11, when water is saturated with carbon dioxide in the presence of solid calcium carbonate and sulphate. No end-point for calcium hydrogen carbonate was obtained in the electrometric titration of calcium hydroxide with carbon dioxide or in the titration of calcium carbonate with sulphuric acid. The equilibrium of the system calcium carbonate–calcium sulphate–carbon dioxide determines the hydrogen-ion concentration in ground waters found in contact with calcareous soils containing gypsum. The importance of this equilibrium to the corrosion of iron pipes laid in the earth is discussed.

J. F. S.

Polarimetric Estimation of Acidic and Basic Groups of Various Compounds. II. J. GROOT (*Biochem. Z.*, 1923, **139**, 188—198).—The fall of rotation of dextrose under the influence of alkali follows the unimolecular law. For normalities of potassium hydroxide between 0 and 0·237*N*, it is found that the velocity constant is proportional to the concentration of alkali. The velocity constant was then determined in the presence of phloroglucinol and alkali, and from this the alkali inactivated by the phloroglucinol could be calculated. Phloroglucinol behaves as a dibasic acid. H. K.

Detection of Chlorine and Bromine in the Presence of Closely Related Ions. M. DIMITROFF (*Z. anal. Chem.*, 1923, **62**, 451—452).—Chlorine-ions can be detected in the presence of bromine-, iodine-, cyanogen-, and thiocyanogen-ions by treating the solution with potassium permanganate and driving the liberated halogens by means of a stream of air through 3—4 c.c. of water containing 0·025 g. of potassium bromide. This solution is then evaporated to 1 to 2 c.c. and 6 c.c. of 2% sodium bromate solution

and 6 c.c. of $5N$-sulphuric acid are added. Air is passed through the liquid to expel the free bromine, and 25 c.c. of water and a few drops of 3% silver nitrate solution are added; a white turbidity shows the presence of chlorine if more than 0·025 mg. of chloride was present in the original solution.

Bromine-ions are detected by treating the original solution as described above and expelling the liberated halogens by means of air into 4—5 c.c. of water containing 0·025 g. of potassium iodide. This solution is boiled whilst passing a stream of air through it, cooled, treated with a few drops of chlorine water, and shaken with a little chloroform or carbon disulphide. A brown upper layer proves bromides to be present in the original solution. A. R. P.

Detection of Chlorate and Bromate in Mixtures of Halogenates, Qualitative Investigation of Such Mixtures, and Application of the Process in Testing Chlorates and Iodates for the Presence of Bromate. M. DIMITROFF (*Z. anal. Chem.*, 1923, **62**, 453—455).—Zinc and sulphuric acid reduce chlorates in the cold quantitatively to chlorides; with bromates and iodates the free halogen is liberated and subsequently reduced by the nascent hydrogen. In hot solutions, the second reaction does not take place, as the iodine and bromine distil off. To test for chlorate in the presence of the other compounds, therefore, 5 c.c. of the solution are boiled with 50 c.c. of $2N$-sulphuric acid and two or three pieces of granulated zinc until all free halogen is expelled. If the resulting solution gives a white turbidity with silver nitrate chlorates were originally present. To detect bromates in a mixture of halogenates, 5 c.c. of the solution are treated with 5 c.c. of 1 : 1-sulphuric acid and 1 c.c. of chloroform. A 0·5% alcoholic iodine solution is then dropped in slowly with constant shaking; in the presence of bromate, the original rose-red colour of the chloroform turns brown. A. R. P.

Use of Bromate in Volumetric Analysis. III. Estimation of Bromate in the Presence of Ferric Iron. G. FREDERICK SMITH (*J. Amer. Chem. Soc.*, 1923, **45**, 1666—1675; cf. this vol., ii, 504, 573).—The estimation of bromates in the presence of ferric iron has been investigated, and three methods are put forward for this estimation. The methods have been tested and their application has been demonstrated. They are: (i) Iodometric method. Phosphoric acid solutions containing sodium pyrophosphate, in which the dissociation of the resulting iron complex to give ferric-ions is less than in the presence of either reagent alone, are analysed for their content of bromate by the addition of potassium iodide in excess and titration of the liberated iodine after two to three minutes with sodium thiosulphate. The time rate of reduction of bromate by potassium iodide with various concentrations of phosphoric acid has been determined and the necessary variation in the concentration of phosphoric acid and sodium pyrophosphate with increasing amounts of ferric iron has been evaluated. (ii) Oxalate–permanganate method. The bromate is reduced by excess of sodium oxalate in boiling sulphuric acid

solution in the presence of mercuric perchlorate and the excess of oxalate determined by titration with potassium permanganate. It is shown that this reaction furnishes the basis of an improved method for iodometric standardisation, using sodium oxalate as the primary standard. (iii) Ferrous sulphate–permanganate method. This involves the same procedure as in the last method, except that ferrous sulphate is substituted for sodium oxalate and the titration is effected in a cold instead of in a hot solution. J. F. S.

Chronometric Estimation of Iodine in Soluble Iodides. EM. RIEGLER (*Bul. Soc. Chim. România*, 1923, **5**, 3—5).—Ten c.c. of the iodide solution are placed in a test-tube and 5 drops of 2% sodium nitrite solution, 5 drops of starch solution, and 5 drops of dilute sulphuric acid are added successively; the contents of the tube are mixed, 1 c.c. of a 2% ethyl acetoacetate solution is added and the time required for the absorption of the liberated iodine is noted by means of a stop-watch. The iodide solution should contain between 0·2 and 1·0 mg. of iodine per 10 c.c.; within these limits, the rate of absorption of the iodine is directly proportional to the quantity of iodine, that is, 0·2 mg. is absorbed in ten seconds and 1·0 mg. in fifty seconds. W. P. S.

Winkler's Titration of Iodides. I. M. KOLTHOFF (*Pharm. Weekblad*, 1923, **60**, 841—845).—Winkler's method is not accurate in presence of bromides, but this difficulty may be overcome by using bleaching powder solution in place of chlorine water for the oxidation, the effect on bromides being dependent on the acidity of the solution. The correct hydrogen-ion concentration is obtained by the addition of succinic acid. Accurate results can be obtained in presence of large excess of bromide. If iron only is present besides iodide, phosphoric acid may be used for the estimation. Organic matter interferes. S. I. L.

Detection of Iodates in the Presence of Chlorates, Bromates, Dichromates, Nitrates, and Similar Salts. M. DIMITROFF (*Z. anal. Chem.*, 1923, **62**, 452—453).—Five c.c. of the solution are shaken with 2 to 3 drops of starch solution, 5 drops of dilute sulphuric acid, and 1 drop of a 0·5% solution of sodium thiosulphate. A deep blue iodine–starch colour proves the presence of iodate. The test may also be applied by mixing the first two reagents, then adding 1 to 2 c.c. of the thiosulphate solution so as to give two layers. A blue ring is then obtained at the interface in the presence of as little as 0·05 mg. of an iodate. A. R. P.

Estimation of Sulphur and some of its Compounds. J. M. TAYLOR (*J. Soc. Chem. Ind.*, 1923, **42**, 294—297T).—The estimation of sulphates by precipitation as barium sulphate is most trustworthy when the sulphate solution and barium chloride solution are added slowly and simultaneously to boiling water acidified with hydrochloric acid. Precipitation from strongly acid solution also yields a pure form of barium sulphate. Methods are described for the analysis of native sulphur, sulphur chloride, chlorosulphonic acid, and thionyl chloride. W. P. S.

Errors in the Estimation of Hydrogen Sulphide. FRED H. HEATH and FRANK A. LEE (*J. Amer. Chem. Soc.*, 1923, **45**, 1643—1647).—The methods of estimating hydrogen sulphide in natural waters have been investigated, and it is shown that the presence of small quantities of salts such as nitrites, nitrates, and alkali salts generally introduce large errors into the iodometric estimation of hydrogen sulphide. It is therefore suggested that this method of estimating hydrogen sulphide in natural water be abandoned and that the colorimetric method of Mecklenburg and Rosenkränzer in which methylene-blue is formed be substituted (A., 1914, ii, 380). The need of a qualitative as well as a quantitative method is further shown by the fact that some samples of water gave no reaction by this latter method, but positive results were obtained by the iodometric method. J. F. S.

Detection of Sulphates in the Presence of Ferric Salts. FRIEDRICH L. HAHN (*Ber.*, 1923, **56**, [*B*], 1733).—It is shown that the delicacy of the barium reaction for sulphates is much impaired in the presence of ferric salts, but that reduction of the latter by means of hydrazine or hydroxylamine enables the detection of the sulphate-ion to be made with certainty. Without reduction, it is impossible to detect less than 0·1% SO_3 in 0·4—0·8 g. Fe_2O_3, but with preliminary reduction, as little as 0·02% may be detected. Neither aluminium nor chromium salts affect noticeably the delicacy of the test for sulphates. H. H.

Estimation of Persulphuric Acids. R. WOLFFENSTEIN and V. MAKOW (*Ber.*, 1923, **56**, [*B*], 1768—1771).—A method for the estimation of hydrogen peroxide, Caro's acid, and persulphuric acid in a mixture of all three is described. The total active oxygen is determined by the addition of a known amount of a ferrous salt and back titration of the excess with potassium permanganate. The hydrogen peroxide is estimated by direct titration with permanganate. The difficulty arises in the attempt to differentiate between Caro's acid, $HO{\cdot}SO_2{\cdot}O{\cdot}OH$, and persulphuric acid, $HO{\cdot}SO_2{\cdot}O{\cdot}O{\cdot}SO_2{\cdot}OH$. The former liberates iodine instantaneously from potassium iodide, whilst the latter requires a considerable time. In practice, however, it is found that the hydrolytic change of persulphuric acid into Caro's acid during the titration of the latter is sufficient, unless precautions are taken, to impair the accuracy of the results. In order to arrest this hydrolysis, the solution must be kept cool and as acid as possible.

The above method estimates persulphuric acid only by difference. A direct method for the estimation of all three peroxide components is as follows. The hydrogen peroxide is first titrated with permanganate. Then sodium acetate is added to the solution until it contains free acetic acid, and the Caro's acid is estimated by titration with sodium sulphite, using iodine as indicator. Finally, the persulphuric acid is estimated by warming with a ferrous salt and titrating the excess of the latter with permanganate. The results may be checked by an estimation of the total active oxygen. H. H.

Analysis of Hydrogen for Traces of Nitrogen. R. L. Dodge (*J. Amer. Chem. Soc.*, 1923, **45**, 1688—1691).—A modification of the usual method for the estimation of hydrogen by combustion over copper oxide has been devised and applied to the analysis of hydrogen for traces of nitrogen. The method consists in drying the hydrogen and admitting it to a system evacuated to 0·01 mm. of mercury. As the gas enters the system it passes along a column of copper oxide 34 cm. long heated to a maximum temperature of 400°. The water formed is condensed in a graduated glass tube which is immersed in ice, and the unburnt gas circulated back through the copper oxide tube. After the whole of the hydrogen is burnt, the residual gas is pumped into a water-jacketed burette and measured. The method is accurate to 0·005%. J. F. S.

Behaviour of Nitro-derivatives of Aromatic Hydrocarbons in Kjeldahl's Process. B. M. Margosches and W. Kristen (*Z. ges. Schiess. Sprengstoffw.*, 1923, **18**, 73—76).—The results of the treatment of a number of nitro-derivatives of aromatic hydrocarbons by various modifications of Kjeldahl's process are given in a series of tables. In no case was the theoretical percentage of nitrogen obtained, owing to the volatilisation of the nitro-compound during the digestion. Tests were carried out with 20 c.c. of sulphuric acid alone, and with the addition of 10 g. of potassium sulphate, 0·5 g. of copper sulphate, 0·5 g. of mercuric oxide and also with the simultaneous addition of copper sulphate and mercuric oxide. The reduction of the period of digestion necessary by the addition of copper sulphate or mercuric oxide is very marked. H. C. R.

Influence of the Method of Precipitation of Proteins on the Results of the Estimation of Total Non-protein Nitrogen in Blood, Plasma, and Corpuscles. P. Cristol and S. Nikolitch (*Bull. Soc. Chim. biol.*, 1923, **5**, 469—486).—Detailed results are presented of a large number of estimations of the non-protein nitrogen in blood plasma and corpuscles, using metaphosphoric acid, tungstic acid, or trichloroacetic acid as protein precipitant. The acidity of the filtrate appears to exert considerable influence on the result. Highest values for non-protein nitrogen are obtained with filtrates of low acidity, whichever precipitant is used. With filtrates of high acidity, the results obtained with the different precipitants diverge considerably. E. S.

Micro-Kjeldahl Methods in the Tanning and Gelatin Industries. O. Gerngross and W. E. Schaefer (*Z. angew. Chem.*, 1923, **36**, 391—394).—An improved micro-Kjeldahl apparatus based on that of Bang is described and illustrated, together with a micro-burette capable of being read to 0·001 c.c. In leather or bone meal analyses, 0·5—1·0 g. of the sample is taken for the preliminary digestion, the contents of the flask diluted to 250 c.c., and 1 c.c. of this solution taken for distillation in the micro-apparatus. When dealing with dilute albuminous solutions such as are met with in the gelatin industry, 1 c.c. of the carefully homogenised solution may be taken directly for the digestion with 2 c.c. of concentrated

sulphuric acid and 3 drops of 10% copper sulphate. The digestion is in such cases complete in thirty to forty minutes. The precautions necessary in the distillation and titration are fully described. The titration may be carried out iodometrically after adding potassium iodide and potassium iodate, or by using a 1% alcoholic solution of *p*-nitrophenol as indicator, which is sensitive to 0·01 c.c. of *N*/80-sodium hydroxide, but cannot be used by artificial light.
H. C. R.

Method for the Estimation of Ammonia in Urine. MALTE LJUNGDAHL (*Compt. rend. Soc. Biol.*, 1922, **87**, 1414—1416; from *Chem. Zentr.*, 1923, ii, 556).—By rapid distillation with steam, the whole of the ammonia in (1 c.c. of) urine may be obtained in three to four minutes. Continuation of the distillation to ten minutes results in an increase of 0·05—0·09 mg. of ammonia obtained. The results obtained agree with those by the Folin method. The ammonia is collected in 2 c.c. of 0·1*N*-sulphuric acid and titrated with 0·1*N*-sodium hydroxide, using methyl-red as indicator. G. W. R.

Formation of Glucoheptonitrile in Urines containing Sugar and Cyanides as Cause of Error in the Estimation of Ammonia. Value of Schaffer's Sodium Carbonate Method. W. MESTREZAT and (MLLE) M. JANET (*Bull. Soc. Chim. biol.*, 1923, **5**, 464—468).—In the estimation of ammonia in urine by Schlœsing's bell method (cf. A., 1922, ii, 453), high results are obtained if large quantities of sugar are present in the urine. This is due to hydrolysis of the nitrile formed by interaction of the hexose and the mercuric cyanide used as antiseptic. Good results may, however, be obtained with such urines if sodium carbonate is used in place of milk of lime according to the technique of Schaffer. E. S.

The Estimation of Ammonia and Urea in Urine and other Fluids. SAMUEL LEVY-SIMPSON and DENIS CHARLES CARROLL (*Biochem. J.*, 1923, **17**, 391—402).—The method is based on the fact that when a mixture of urea and ammonia is distilled with steam and alcohol, only ammonia comes over during a certain stage of the distillation. Using 5 to 10 c.c. of the liquid and 90 c.c. of alcohol, it is found that all the ammonia distilled before frothing commenced. Details of the conditions under which accurate results can be obtained by this method are given. The method, which is claimed to be accurate, has the advantage of being rapid. An ammonia determination requires seven minutes, whilst a complete determination of ammonia and urea can be made with one apparatus in thirty minutes.
S. S. Z.

Decomposition of Carbamide and other Nitrogenous Compounds during the Distillation of Urine with Steam. MALTE LJUNGDAHL (*Compt. rend. Soc. Biol.*, 1922, **87**, 1411—1413; from *Chem. Zentr.*, 1923, ii, 556).—In the estimation of ammonia in urine by distillation with steam, if a rapid current is employed the whole of the ammonia comes over within four minutes, whilst a longer time is required for the decomposition of carbamide and glycine.
G. W. R.

A Micro-method for Estimating the Total Phosphoric Acid in Blood and Fæces. WERNER GROTE (*Z. physiol. Chem.*, 1923, **128**, 254—256).—The phosphoric acid content of blood and of fæces may be estimated by destroying the organic matter with nitric acid and sulphuric acid, precipitating the phosphoric acid with ammonium molybdate, and estimating the ammonium in the filtrate as in Kjeldahl's method. It is found that each c.c. of $N/70{\cdot}2$-hydrochloric acid used up by the ammonia distilled over corresponds with 0·00021 g. of P_2O_5 instead of with 0·000337 g., the value obtained by calculation from the formula

$(NH_4)_3PO_4,12MoO_3,12H_2O$. W. O. K.

Estimation of the Carbon Content of Solutions. JOSEPH NEEDHAM (*Biochem. J.*, 1923, **17**, 431—434).—The solution is burned in a silica boat placed in a quartz combustion tube. The carbon dioxide is caught in a receptacle containing baryta, from which solution it is liberated by the addition of tartaric acid and is estimated in a Haldane gas measuring apparatus. S. S. Z.

The Estimation of Carbon Monoxide in Vitiated Air. F. S. SINNATT and L. SLATER (*Lancs. Cheshire Coal Res. Assoc. Bull.*, 1923, No. 13).—A modification of the apparatus of Winmill (T., 1914, **105**, 1996) and Graham (A., 1919, ii, 117) is described, and its applications and those of the methods of Graham (*loc. cit.*) and Sinnatt and Cramer (A., 1914, ii, 383) are discussed in detail.

T. S. W.

Bicarbonate Equilibrium. J. W. SHIPLEY and IVAN R. MCHAFFIE (*J. Soc. Chem. Ind.*, 1923, **42**, 319—326T).—From data obtained in the electrometric titration of calcium hydroxide by carbon dioxide (see this vol., ii, 649), the condition of calcium hydrogen carbonate has been investigated. It is shown that the degree of hydrolysis of calcium carbonate in water at 20° is 10%. The solubility product of calcium hydroxide at 20° as calculated from the electrometric titration was found to be $0{\cdot}64\times10^{-5}$. Electrometric titrations of sodium carbonate and calcium carbonate in very dilute solutions were carried out in a closed electrode vessel, using hydrochloric acid as the titrating acid. A new constant, $H^{\cdot}\times CO_3''=5\times10^{-13}$, was found to hold for carbonate equilibria. The primary constant, $k_1=H^{\cdot}\times HCO_3'/H_2CO_3$, decreases with dilution, and the secondary constant, $k_2=H^{\cdot}\times CO_3''/HCO_3''$, increases on dilution, but the product, $H^{\cdot}\times CO_3''$, remains constant. The proportion, n, of the total carbon dioxide in solution existing as molecular carbonic acid, H_2CO_3, has been calculated and a curve constructed showing the variation of this proportion with dilution. This variation is directly proportional to the dilution. J. F. S.

Colorimetric Estimation of Small Quantities of Metals in Foodstuffs and the Preliminary Destruction of the Organic Matter. K. K. JÄRVINEN (*Z. Unters. Nahr. Genussm.*, 1923, **45**, 183—190).—Details of a method for the destruction of the organic matter in foodstuffs, preparatory to the colorimetric estimation of small quantities of metals are given. The organic

matter is oxidised with strong nitric acid (d 1·40) in a Kjeldahl digestion flask. Sulphuric acid is added after a preliminary oxidation with nitric acid alone. Oxides of nitrogen are afterwards removed by dilution with water and boiling and sulphites by the addition of sodium thiosulphate and burning off the sulphur precipitated. Ten g. of organic dry matter can be completely destroyed in one to three hours and the method is suitable for use in estimating all metals except mercury, which is volatilised during the destruction of the organic matter. Details of colorimetric methods of estimating a few mg. of the following metals in 100 g. of foodstuffs are given: tin and lead in the presence of one another, copper and zinc in the presence of one another, aluminium, nickel, arsenic (in carpets, etc.), and antimony. The methods depend on the colour developed by passing hydrogen sulphide or adding sodium sulphide to the solution containing the metal after the removal of all organic matter and oxidising and reducing substances, and comparing it with the colour of a standard solution of the same metal treated under exactly similar conditions. The deposition of finely divided sulphur is prevented by the addition of 50% alcohol. Very accurate results were obtained in this way. H. C. R.

Microscopic Characterisation of the Picrates and Tartrates of Potassium and Sodium. ED. JUSTIN-MUELLER (*J. Pharm. Chim.*, 1923, [vii], **28**, 15—17).—The picrates of potassium and sodium, although similar macroscopically, are easily distinguishable microscopically, sodium picrate forming slender, yellow needles and potassium picrate long, yellow prisms. With tartaric acid, potassium salts give a precipitate visible to the naked eye only at a certain concentration, whilst with sodium salts the tartrate formed is never visible macroscopically. The salt formed may, however, be identified by microscopic examination of the sediment after standing or centrifuging. Potassium tartrate forms abundant lozenges, sodium tartrate octagonal plates and clinorhombic prisms. Sketches of the crystals are given. W. T. K. B.

The Kramer-Tisdall Method for the Estimation of Calcium in Small Amounts of Serum. FREDERICK F. TISDALL (*J. Biol. Chem.*, 1923, **56**, 439—441; cf. A., 1921, ii, 595).—Removal of the supernatant fluid from the calcium oxalate precipitate by decantation is simpler than using a siphon as originally described. E. S.

Analysis of Calcium Phosphate. ROKURO NAKASEKO (*Mem. Coll. Sci. Kyoto*, 1923, **6**, 157—164).—A method for the simultaneous estimation of calcium and phosphoric acid in calcium phosphate is described. The calcium is precipitated as oxalate from an acetic acid solution, and the phosphoric acid in the filtrate from the calcium oxalate is precipitated as ammonium manganese phosphate after the excess of oxalic acid has been destroyed by the addition of the requisite quantity of potassium permanganate. Secondary and tertiary phosphates in a mixture may be estimated by titration with N/10-acid, using methyl-orange as indicator. The titration of primary calcium phosphate, after it has been rendered neutra

towards methyl-orange with standard alkali solution, using phenolphthalein as indicator, yields untrustworthy results. W. P. S.

Estimation of Barium as Oxalate. BARBU N. ANGELESCU (*Bull. Soc. Chim. România*, 1923, **5**, 12—15).—A solution containing from 0·20 to 0·25 g. of the barium salt is mixed with three times its volume of alcohol, and ammonium oxalate solution is added. The mixture is heated on a water-bath for fifteen minutes and, after a further sixty minutes, the precipitated barium oxalate is collected on a filter, washed with 75% alcohol, dried at 70°, and weighed; 0·002 g. is added to the weight found as an allowance for the solubility of the barium oxalate. W. P. S.

Detection and Estimation of Mercury in Gauze Dressings. ET. BARRAL (*J. Pharm. Chim.*, 1923, [vii], **28**, 49—51).—In order to effect complete solution of the mercury the gauze is heated with eight to ten times its weight of dilute aqua regia containing 10% of strong hydrochloric acid and 2% of strong nitric acid. The warm liquid is filtered and evaporated nearly to dryness. Evaporation must be carried out at room temperature (or a maximum of 40—45°) to avoid loss of mercuric chloride by volatilisation. The slightly moist residue is tested with (*a*) stannous chloride, (*b*) diphenylcarbazide in benzene solution (after neutralising with a little sodium hydrogen carbonate), (*c*) potassium iodide, sodium carbonate, and ammonia, and (*d*) hydrogen sulphide. The above method of extraction may also be employed for the estimation of the merury present in the gauze, but an accuracy greater than 5% is not obtainable. W. T. K. B.

Colorimetric Methods with the Aid of Wilhelm Ostwald's Colour Standards. F. V. VON HAHN (*Z. angew. Chem.*, 1923, **36**, 366—369).—By the application of the Ostwald colour standards, colorimetric analysis is simplified and the necessity for preparing and keeping a number of standard colour solutions obviated. A known thickness of the coloured solution, contained in a cell, is illuminated from below by normal white light of the same intensity as that falling on the colour scale, and the two are viewed simultaneously through a tube into which a suitable colour filter can be inserted. By varying the filter and comparing with the standard colour scale, the colour of the solution is analysed into its components and so characterised. Details and tables for the colorimetric estimation of copper (as cuprammonium or potassium copper ferrocyanide), manganese (as permanganic acid), and lead (as colloidal lead sulphide) are given, and a "colorigram," with a triangular system of co-ordinates, drawn. The light used may with advantage be polarised, especially when artificial light is employed. W. T. K. B.

Detection and Separation of Indium. ISABURO WADA and SUNAO ATO (*J. Chem. Soc. Japan*, 1923, **44**, 1—36).—When the residue obtained by evaporation of an aqueous solution of indium nitrate is heated at 120° during one hour, the element does not form any dehydrated compound insoluble in nitric acid,

thus differing from the metals of the tungsten and columbium group. Indium cannot be separated from other elements by distillation of the bromide from its hydrobromic acid solution, or by precipitation of its chloride. In neutral solution, indium is completely precipitated by hydrogen sulphide, even when it is present alone. When mixed with the elements of the hydrogen sulphide group, indium is largely precipitated by hydrogen sulphide if the concentration of the acid in the solution is less than $0{\cdot}3N$, but to a very slight extent only if the concentration is $0{\cdot}6N$. In $0{\cdot}6N$-acid solution the elements of the hydrogen sulphide group are nearly completely precipitated by sufficient excess of hydrogen sulphide, only a small quantity, with practically all the indium, remaining in the filtrate. From this filtrate on dilution with an equal volume of water all the elements of the hydrogen sulphide group are completely precipitated with a very small quantity of indium. The indium present in the precipitate is separated together with bismuth from the other metals. Platinum, iridium, rhodium, ruthenium, etc., are not completely precipitated under the same conditions, but are precipitated on heating the solution (acidity $1N$), after saturation with hydrogen sulphide, in a pressure bottle in boiling water for one hour. The bismuth can be almost completely separated from indium by hydrolysis, the small quantity remaining in solution being precipitated as sulphide from $0{\cdot}6N$-acid solution. Indium behaves like titanium and zirconium with ammonia and ammonium sulphide, sodium hydroxide, peroxide, or carbonate or treatment with ether. It can be separated from the two elements by means of tartaric acid, ammonia, and ammonium sulphide. K. K.

Treatment of Permanganate Solutions for Volumetric Analysis. G. Bruhns (*Chem. Ztg.*, 1923, **47**, 613—615; cf. A., 1906, ii, 577).—A discussion of the preparation and use of standard solutions of potassium permanganate for volumetric analysis, with reference to their stability. A. A. E.

Titration of Solutions of Permanganate and Sodium Arsenite. William T. Hall and Carl E. Carlson (*J. Amer. Chem. Soc.*, 1923, **45**, 1615—1620).—The estimation of manganese in steel by the method of oxidation to permanganate and titration with sodium arsenite solution has been investigated. It is shown that under the conditions which usually prevail in the analysis of steel, the electrometric titration of permanganate with sodium arsenite solution causes the manganese to be reduced from a valency of seven to an average valency of 3·3 when the bismuthate method is used. This result is in agreement with the results of Rose (A., 1919, ii, 36) and Geloso (A., 1921, ii, 115). The reaction may be expressed $6MnO_4' + 11H_2AsO_3' + 15H^{\cdot} \rightarrow 2Mn^{\cdot\cdot\cdot\cdot} + 4Mn^{\cdot\cdot\cdot} + 11HAsO_4'' + 13H_2O$. The reduced condition corresponds with an oxide, Mn_3O_5, but it is improbable that such an oxide actually exists. The colour of the solution indicates the presence of tervalent manganese and the fact that manganese dioxide often separates on keeping shows that the quadrivalent manganese readily assumes the condition of colloidal dioxide and finally forms the gel. Probably this reaction takes place

thus: $2Mn^{\cdot\cdot\cdot\cdot}+4Mn^{\cdot\cdot\cdot}+8H_2O \rightarrow 2Mn^{\cdot\cdot}+4MnO_2+16H^{\cdot}$. The fact that halide causes a more complete reduction of the manganese is in accord with the usual behaviour of hydrogen halide in permanganate titrations. It prevents the formation of colloidal dioxide and keeps the manganese in a more reactive condition. The electrometric titrations show that when arsenite is titrated with permanganate in 2·5N-sulphuric acid solution the manganese is reduced to an average valency of 2·5, $4MnO_4'+9HAsO_3''+14H^{\cdot} \rightarrow 2Mn^{\cdot\cdot}+2Mn^{\cdot\cdot\cdot}+9HAsO_4''+7H_2O$. Whenever the reaction between permanganate and arsenite is used in practice to determine either manganese or arsenic, it is important to direct attention to such details as temperature, acid concentration, and presence of halide or manganous salt, and to standardise the solutions under exactly the same conditions as prevail in the analysis. J. F. S.

Alleged Influence of Silicic Acid Hydrosol on the Volumetric Estimation of Iron in Hydrochloric Acid Solution. L. Brandt (*Z. anal. Chem.*, 1923, **62**, 417—450).—The alleged action of silicic acid hydrosol in inhibiting the oxidation of hydrochloric acid by permanganate in titrations of iron has been completely investigated anew (cf. Schwarz and Rolfes, A., 1919, ii, 170; Schwarz, A., 1919, ii, 480; 1920, ii, 389; Brandt, A., 1919, ii, 373, 428; 1920, ii, 269). It has now been found that commercial water-glass contains oxidisable impurities which tend to give erratic results, but the addition of a pure silicic acid sol made from silicon tetrachloride has no inhibiting action on the liberation of small amounts of free chlorine in side reactions. It is definitely proved that the addition of silicic acid sol has no influence on the results obtained in titrating ferrous chloride with permanganate either in the presence or absence of manganese sulphate.

A. R. P.

Gravimetric and Volumetric Methods for the Estimation of Tin in Alloys. Antonín Jílek (*Chem. Listy*, 1923, **17**, 24—27; cf. this vol., ii, 186, 436).—The stannic oxide obtained in the analysis by Czerwek's method of tin alloys does not adsorb copper or lead salts, but can adsorb considerable quantities of antimony, particularly if potassium is present in solution. Thus the addition of potassium antimonyl tartrate to the solution from which the stanniphosphate is precipitated gives results which may be as much as 17·5% high. This error can be diminished by thorough washing of the stanniphosphate with a solution of the same composition as that recommended by Czerwek for the solution of bearing metal, instead of dilute nitric acid, which he used. With the modified method, results obtained are 1% high for alloys containing above 60% of tin, accurate for alloys containing about 14% of tin, and low for those containing less tin than this. R. T.

New Characteristic Microchemical Reaction for the Detection of Antimony and Tin. Andrei P. Ortodocsu and (Mlle) Marcelle Ressy (*Bull. Soc. chim.*, 1923, [iv], **33**, 991—994).—A drop of the solution under investigation is placed on a microscope

slide side by side with a drop of a solution of sodium chloride containing 17 g. per litre. The drops are made to coalesce and are allowed to crystallise. The presence of tin is indicated by the appearance of six-pointed stars of the composition $2SnCl_2,3NaCl$. Antimony appears as four-pointed stars of the composition $SbCl_5,NaCl$. The forms are quite characteristic and distinctive, and are given by no other common metal. H. H.

The Electrolytic Estimation of Antimony. A. LASSIEUR (*Compt. rend.*, 1923, **177**, 263—265).—Hitherto all estimations of antimony by the electrolytic method have given incorrect values (cf. Henz, A., 1904, ii, 150). The error may be avoided by using a platinum electrode on which mercury has been electrolytically deposited. The difference of electrode potentials should be of the order of 1·3 volts, and the deposit then obtained is of good adherence and may be dried at 100° for weighing. The author suggests that the excessive values obtained when antimony is deposited directly on the platinum are due to the hydrogenating properties of the latter element. H. J. E.

Hexamethylenetetramine as a Reagent in Microscopic Qualitative Chemical Analysis. HOWARD IRVING COLE (*Philippine J. Sci.*, 1923, **22**, 631—637).—Solutions in hydrochloric acid of salts of antimony, bismuth, cadmium, gold, iridium, mercury, palladium, platinum, tin, and silver (in nitric acid solution) give characteristic crystalline precipitates with hexamethylenetetramine, whilst solutions of salts of antimony, bismuth, cadmium, palladium, platinum, and tin also give characteristic precipitates, usually at greater dilutions, if potassium iodide is added as well as hexamethylenetetramine. Crystalline compounds not sufficiently characteristic for identifying the metals are also formed in the presence of calcium, iron, magnesium, manganese, and titanium. Hydrochloric acid, nitric acid, and sulphuric acid alone give crystalline precipitates with hexamethylenetetramine and potassium iodide, but the crystals are easily distinguished from those formed in the presence of any of the above metals. The procedure recommended for applying the test is to add a fragment of solid hexamethylenetetramine to a drop, 2—4 mm. in diameter, of the solution to be tested, and then to examine the solution under a low-power microscope, a fragment of potassium iodide being added subsequently if necessary. A description is given of the shape, colour, and effect on polarised light of the characteristic crystalline compounds, and photographs of most of them are reproduced. The test is most sensitive with antimony and bismuth, the addition of potassium iodide enabling these metals to be identified at dilutions of 1 : 15,000 and 1 : 100,000, respectively. L. A. C.

Titration of Very Small Amounts of Gold. W. B. POLLARD (*Bull. Inst. Mining Met.*, 1923, **223**).—For the estimation of quantities of gold up to 5 mg., the metal is dissolved in 2 c.c. of aqua regia, the liquid being carefully boiled, the flask meanwhile being rotated, until only one or two drops remain. In order to avoid

deposition of gold after dilution, nitrous acid must be removed by the addition of 2 c.c. of 1% paraldehyde solution, the fumes blown out of the flask, and the liquid allowed to remain for two minutes. Twenty-five c.c. of water are then added, together with 1 c.c. of a 0·1% solution of *o*-tolidine in 10% hydrochloric acid, and a small quantity of a dilute solution of silver nitrate as catalyst. The liquid is then titrated with 0·01*N*-*p*-methylaminophenol sulphate in 2% hydrochloric acid, the mixture finally being gently heated. Titration may be repeated on the same sample after evaporation to dryness, treatment with aqua regia, and repetition of the process. In the presence of iron, ammonium fluoride must be added; large quantities of copper cause somewhat high results. With the *o*-tolidine reagent, it is possible to detect gold by the development of a yellow or brown colour at a dilution of 1 in 2×10^7.

CHEMICAL ABSTRACTS.

Estimation of the Easily Dehydrated Alcohols in Essential Oils. L. S. GLICHITCH (*Compt. rend.*, 1923, **177**, 268—270).—The estimation of such alcohols as linalool and terpineol by acetylation with subsequent estimation of the ester formed is inaccurate owing to the incompleteness of the first stage by reason of the dehydration of a portion of the alcohol. Dilution of the reaction mixture with an inert solvent (Boulez, A., 1907, ii, 306; Schimmel & Co., A., 1907, ii, 782) diminishes but does not eliminate the error. By treatment of the alcohols with a mixture of acetic anhydride and formic acid at the ordinary temperature the alcohols are converted into formates (cf. Béhal, A., 1899, i, 734; 1900, i, 580) and these may be employed to obtain correct values by saponification in the usual way. Comparative results obtained by the normal method of acetylation, acetylation in presence of xylene, and by the above method are given. H. J. E.

Reaction of α- and β-Naphthol with Sodium. HERMANN KUNZ-KRAUSE (*Chem. Ztg.*, 1923, **47**, 646).—0·01—0·1 G. of the naphthol is dissolved in a few c.c. of absolute alcohol and thin pieces of sodium are dropped in as long as they will dissolve, the tube being cooled in water. In the case of α-naphthol, only a pale bluish-green colour is produced with a faint fluorescence, but with β-naphthol a deep royal blue colour appears, with a bluish-violet fluorescence. Further additions of sodium change the colour to olive-green, brown, and orange, in that order. The fluorescence remains throughout these colour changes. This test is recommended as superior to the ammonia test in aqueous solution for distinguishing between α- and β-naphthol. H. C. R.

Rapid Reduction Method for the Estimation of Sugar in Blood. G. DENIGÈS (*Compt. rend. Soc. Biol.*, 1922, **87**, 1283—1285; from *Chem. Zentr.*, 1923, ii, 607—608).—The use of trichloroacetic acid for the removal of proteins from blood prior to estimation of sugar with Fehling's solution is inapplicable. A solution containing 29 g. of sodium chloride in 71 g. of water containing 10% of trichloroacetic acid is recommended for this purpose.

After adding this solution to an equal volume of blood or serum the mixture is shaken and placed for three minutes on a boiling water-bath. After clarifying by centrifuging and making up to the original volume, one-tenth by volume of sodium hydroxide solution is added. The mixture is added to 1 c.c. of boiling Fehling's solution (Bonnans), containing ferrous cyanide and the boiling continued. For the completion, if necessary, of the reduction of the Fehling's solution, a solution of dextrose containing 0·36 g. in 10 c.c. of water is used. The reaction is not affected by the precipitate of calcium phosphate obtained on neutralisation.

G. W. R.

Inositol. I. A Method of Estimation. JOSEPH NEEDHAM (*Biochem. J.*, 1923, **17**, 422—429).—The tissues are extracted with dilute aqueous acetone, and from this the inositol is precipitated with a saturated basic lead acetate solution. The precipitate is then decomposed with hydrogen sulphide, filtered, and the inositol in the filtrate is further precipitated with alcohol and is estimated by determining the carbon in it, utilising the author's micro-method (cf. this vol., ii, 655). Inositol of ox muscle is identical with that produced by the hydrolysis of phytin. S. S. Z.

Comparative Experiments on the Different Methods of Estimating Maltose formed by the Fission of Starch. K. JOSEPHSON (*Ber.*, 1923, **56**, [*B*], 1758—1761).—The results obtained by Bertrand's method in following the course of the fission of starch by amylase are uniformly trustworthy; the process does not appear to be inferior to the hypoiodite method of Willstätter and Schudel (A., 1918, ii, 337). The main advantage of the latter procedure lies in the possibility of estimating aldehydic in the presence of ketonic sugars, if other substances which react with iodine are absent.

In the estimation of maltose in pure aqueous solution, the data obtained by Bertrand's process are uniformly somewhat higher than those obtained by the hypoiodite method. In general, slightly high results are obtained in estimating sugars by Bertrand's solutions which have been preserved during some months. In the estimation of maltose formed by the action of malt amylase on starch, the results obtained by the hypoiodite process are uniformly slightly lower than those by the Bertrand method; it appears possible that a slight, systematic error is inherent to the former procedure. H. W.

Comparison of Methods of Estimating Starch. K. ALPERS and H. ZIEGENSPECK (*Z. Unters. Nahr. Genussm.*, 1923, **45**, 163—174).—Twelve different methods of estimating starch in flours and brans were tested and the results obtained are given in a table. All the methods suffered from certain disadvantages, some being troublesome and some giving inaccurate results. Mayrhofer's gravimetric method (A., 1897, ii, 525) gives accurate results only with pure starches and fails in the case of foodstuffs like flour containing bran or substances yielding pentosans. This method

can, however, be employed in the case of sausage meats containing pure starch, but care must be taken that errors do not arise from the incomplete solution of the starch in the aqueous alkali. A method based on the estimation of the dextrose produced after treating the sample with alcoholic potassium hydroxide is also only applicable to pure starches. This method is preferable to that of Mayrhofer for estimations of starch in sausage meats. The results of estimations of starch in flours and brans by both these methods are much increased by the pieces of husk in the samples. The polarisation methods of Lintner and Belschner and of Evers are recommended on account of their simplicity. It is occasionally difficult to obtain a sufficiently clear solution for the polarimeter in Lehmann and Schowalter's polarisation method. The possible error of polarisation methods is assessed at more than 3%. When estimating starch in sausage meats, the possible decomposition of the starch by ferments and bacteria must not be overlooked.

H. C. R.

Estimation of Lactic Acid in Blood. J. J. R. Macleod [with M. E. Armour] (*J. Lab. Clin. Med.*, 1923, 7, 635—642).—A modification of Fürth and Charnass's method (A., 1910, ii, 807). Proteins are precipitated from 25—50 c.c. of blood mixed with 100 c.c. of 2% hydrochloric acid by the addition of 5% mercuric chloride solution; dilution is followed by filtration and removal of the mercury as sulphide. An aliquot portion is nearly neutralised and evaporated below 40°, and then extracted with ether mixed with sodium hydroxide solution in a Dunbar apparatus, after addition of ammonium sulphate and phosphoric acid. After removal of the ether below 50°, the alkaline sodium lactate is distilled with 0·5% sulphuric acid in presence of potassium permanganate into a standard solution of potassium hydrogen sulphite, which is then titrated against iodine solution. Each 1 c.c. of $0\cdot1N$-iodine solution corresponds with 0·05 c.c. of $0\cdot1N$-lactic acid.

Chemical Abstracts.

Some Causes of Error in the Estimation of β-Hydroxybutyric Acid. Ch. O. Guillaumin (*Bull. Soc. Chim. biol.*, 1923, 5, 426—431).—The most practical method for the estimation of β-hydroxybutyric acid is that of Van Slyke (A., 1918, ii, 86). The blank estimation should not be carried out, since the value so obtained is usually due to the oxidation of some of the β-hydroxybutyric acid under the influence of the mercuric reagent. E. S.

A Modified Test for Phthalates, with Particular Reference to the Detection of Ethyl Phthalate. R. E. Andrew (*Ind. Eng. Chem.*, 1923, 15, 838).—Ethyl phthalate is used as a denaturant for alcohol for certain purposes. The resorcinol test as generally given is not trustworthy, since a satisfactory blank cannot be obtained. In carrying out the test, it is necessary to avoid heating after adding acid to the resorcinol mixture. Ten c.c. of the solution to be tested are evaporated with 5 drops of a 10% solution of sodium hydroxide on a steam-bath, 0·5 c.c. of a 5%

solution of resorcinol is added, and the liquid again evaporated to dryness. It is removed from the bath and 6 drops of concentrated sulphuric acid are at once added and mixed thoroughly. When cool, 10 c.c. of water are added and it is transferred to a test-tube with 10 c.c. of wash water; 5 c.c. of 10% sodium hydroxide solution are added, when a green fluorescence will show the presence of phthalate. E. H. R.

Precipitation of Tannic Acid by Gelatin. ARTHUR W. THOMAS and ALEXANDER FRIEDEN (*Ind. Eng. Chem.*, 1923, **15**, 839—841).—Gelatin is completely precipitated by gallotannic acid when the ratio of tannin to gelatin is not less than 2 : 1 and the gelatin-tannin precipitate is not soluble in excess of tannic acid. The optimum hydrogen-ion concentration for gallotannic acid is p_H 4·4—4·6, but there is a definite hydrogen-ion concentration for each sort of vegetable tannin for optimal precipitation. If the solution is not adjusted to near this value, the precipitate may fail to form. The presence of a neutral electrolyte broadens the range of hydrogen-ion concentration for precipitation, but does not increase the sensitiveness of the reaction at the optimum hydrogen-ion concentration. Under the best conditions, tannin can be detected at dilutions as high as 1 : 100,000—200,000, depending on the source of the tannin. The ageing of gelatin solutions has no effect on the sensitiveness in testing for tannin, provided bacterial action is prevented.

H. C. R.

Identification of Cacao Butters by Curves of Miscibility. MARANGE (*Compt. rend.*, 1923, **177**, 191—194).—Extending the work of Louise (A., 1911, ii, 548, etc.), the author studies the miscibility curves for mixtures, with aniline and alcohol, of various pure and adulterated cacao butters, and shows that these curves afford a ready indication as to the purity of the sample examined. E. E. T.

Schiff's Rosaniline–Sulphurous Acid Reaction for Aldehydes. KARL JOSEPHSON (*Ber.*, 1923, **56**, [*B*], 1771—1775).—Schiff's reaction can be applied to aldehydes only under definite conditions with regard to the acidity of the solution; the development of a not too weak violet coloration is regarded as a fairly definite proof of the presence of the aldehydic group.

A red coloration is caused by a number of organic substances, which in all probability do not contain the aldehydic groups. The tint is identical with that of rosaniline solutions. The effect is attributed to the withdrawal of a portion of the sulphurous acid from combination with rosaniline (to form salt-like compounds with the proteins), whereby rosaniline is liberated. A red coloration is also developed when Schiff's solution is treated with phosphate buffer solutions of P_H 4·5—7·8, the maximum intensity being observed at P_H 5·9—6·1. H. W.

The Titration of Sodium Formaldehydesulphoxylate. BERNARD SALKIN (*Ind. Eng. Chem.*, 1923, **15**, 848—849).—Contrary to what has been stated (cf. Heyl and Greer, A., 1922, ii, 288), sodium formaldehydesulphoxylate can be titrated with

ammoniacal copper sulphate or with iodine with concordant results. The method of analysis now described involves three titrations, one with copper sulphate and two with iodine, from the results of which may be calculated the sodium formaldehydesulphoxylate, hyposulphite and hydrogen sulphite–formaldehyde present. In the first titration, the solution of the sample (15 g. in 100 c.c.) is run into a standard solution of copper sulphate (125 g. of crystals per litre) made strongly ammoniacal, at 55° (1 mol. of $CuSO_4 \equiv 0{\cdot}5$ mol. of hyposulphite or 0·5 mol. of sulphoxylate). For the second titration, 25 c.c. of a solution of the sample (6 g. per litre) are titrated with $0{\cdot}1N$-iodine solution, 2 c.c. excess of the iodine solution are added, and after five minutes titrated back with thiosulphate solution. In this case, 1 mol. of iodine$\equiv$1/6 mol. of hyposulphite or 1/4 mol. of sulphoxylate. These two titrations taken together give both hyposulphite and sulphoxylate. In the third titration 50 c.c. excess of $0{\cdot}1N$-iodine solution over that used in the second titration are added to 25 c.c. of the sample solution, followed by sodium hydroxide solution to give a yellow colour. After ten minutes, the solution is acidified and titrated back with thiosulphate. From the number of c.c. of iodine consumed, one and a half times the number of c.c. used in the second titration are subtracted. The difference is the equivalent of the sodium hydrogen sulphite–formaldehyde present. All the titrations must be made in absence of air. E. H. R.

Estimation of Aldehydes and Ketones in Essential Oils. C. T. Bennett and F. C. L. Bateman (*Perf. and Essent. Oils Rec.*, 1923, **14**, 268).—A critical examination of the two methods generally adopted for the estimation of aldehydes and ketones in essential oils, namely the " bisulphite " method and the " neutral sulphite " method. E. M. V.

Some Observations on the Detection of Acetone in Urine. B. A. van Ketel (*Pharm. Weekblad*, 1923, **50**, 833—836).—The methods of Legal and le Nobel are not very sensitive, but the modification of Rotheva gives much better results. The ammonia used must be free from acetone; ammonia often contains traces of acetone, which may be due to its preparation from plant residues or from turf. Acetoacetic acid, which may be present in the urine of persons suffering from diabetes, readily forms acetone, and may thus invalidate the test, but β-hydroxybutyric acid does not give a positive result with the ordinary methods. S. I. L.

Estimation of Acetone and of Ethyl Alcohol in Mixtures of the Two. J. H. Bushill (*J. Soc. Chem. Ind.*, 1923, **42**, 216—218T).—The acetone is estimated iodometrically by the method described by Rakshit (A., 1916, ii, 544); the quantity of alcohol present is calculated from the specific gravity of the mixture after allowance has been made for the acetone. Tables are given, showing the specific gravity of solutions containing small quantities of acetone and alcohol. W. P. S.

Volumetric Estimation of Acetone. AL. IONESCU, (MLLE) ELISE SPIRESCU, and D. POPESCU (*Bul. Soc. Chim. România*, 1923, **5**, 15—21).—Ten c.c. of acetone solution (about 0·5%), 10 c.c. of 50% sulphuric acid, 10 c.c. of mercuric sulphate solution (50 g. of mercuric oxide dissolved in 200 g. of sulphuric acid and diluted to 1 litre), and 100 c.c. of water are boiled together in a reflux apparatus for twenty minutes. The precipitate is then collected on a filter, washed with 200 c.c. of water, transferred to a flask and dissolved by heating with 25 c.c. of a mixture of sulphuric acid and nitric acid (sulphuric acid, 2 parts, nitric acid, 1 part). The solution is treated with a few drops of permanganate solution to destroy nitrous compounds, diluted with 100 c.c. of water, 12 drops of 10% sodium nitroprusside solution are added, and the turbid mixture is titrated with $N/10$-sodium chloride solution, the disappearance of the turbidity denoting the end-point of the titration. Each c.c. of $N/10$-sodium chloride solution is equivalent to 0·0028 g. of acetone; this factor is found by actual experiment with pure acetone and is higher than the theoretical value (0·002348).

W. P. S.

Estimation of Tryptophan. GEORGE E. HOLM and GEO. R. GREENBANK (*J. Amer. Chem. Soc.*, 1923, **45**, 1788—1792).—Some of the difficulties and errors in the various methods previously used are indicated. The effect of temperature and time on the reaction of tryptophan with *p*-dimethylaminobenzaldehyde in 20% hydrochloric acid has been studied. In this concentration of acid, the reaction requires greater time than is generally supposed. Thus at 37° about eight days are necessary. At higher temperatures, the time required for the development of the colour is less, but the colour is then less stable. Pure tryptophan in solution can be accurately estimated by this method (cf. May and Rose, this vol., i, 160). Experiments on casein, fibrin, and Witte's peptone show that the tryptophan content of proteins can also be accurately estimated by this method without previous hydrolysis of the protein, but apparently an enzyme-digested protein is more suitable. There is excellent agreement between the tryptophan content of fibrin as estimated by the colorimetric method (5·00%), and as found by the "humin" formation method (5·05%) of Gortner and Holm (A., 1918, i, 84).

W. S. N.

Estimation of Urea by Urease. GEORGE MACFEAT WISHART (*Biochem. J.*, 1923, **17**, 403—405).—A method based on treating urea with soja bean meal in presence of sodium carbonate and blowing over the ammonia into standard acid. The method is accurate to less than 1%.

S. S. Z.

Estimation of Blood Urea. JEANETTE ALLEN BEHRE (*J. Biol. Chem.*, 1923, **56**, 395—404).—In the estimation of urea in whole blood, considerably higher (50%) results may be obtained when concentrated extracts of soja bean are used than when dilute extracts are employed. This is possibly due to the presence in the soja bean, in small concentration, of a second enzyme which produces

ammonia from some constituent of blood other than urea. This constituent is present mainly in the corpuscles; it does not diffuse through collodion. Blood filtrates, obtained by heat coagulation or by precipitation with tungstic acid, do not give increased values for urea with increased concentrations of extract. E. S.

Application of the Diazotisation of the Benzoyl Group in the Toxicological Detection of Alkaloids. HENRI PECKER (*J. Pharm. Chim.*, 1923, [vii], **28**, 13—15).—Guerbet's method for the detection of alkaloids containing benzoyl groups (cf. A., 1920, ii, 517) is inapplicable in the presence of ptomaines, since the latter alone can give rise to the characteristic orange colour.
W. T. K. B.

Preparation and Comparison of Standards for the Estimation of Creatine and Creatinine. GRAHAM EDGAR (*J. Biol. Chem.*, 1923, **56**, 1—6).—Of the various substances which have been proposed as standards for the estimation of creatine and creatinine by Folin's colorimetric method (A., 1914, *ii*, 505), creatinine zinc chloride and creatinine picrate are considered to be the most suitable since they are readily obtained pure. Creatinine zinc chloride can be readily prepared by fusing commercial creatine with anhydrous zinc chloride. E. S.

Physiology and Pathology of the Bile Secretion. I. Estimation of the Bile Acids in Human Duodenal Bile. F. ROSENTHAL and M. FREIHERR VON FALKENHAUSEN (*Arch. expt. Path. Pharm.*, 1923, **98**, 321—338).—The various methods for the estimation of the bile acids are reviewed and a new method, suitable for clinical use, is described in which the gasometric method of Foster and Hooper (A., 1919, ii, 376) is combined with a sulphur estimation of the alcohol-soluble fraction of the bile. When applied to human bile, the gasometric estimation gives the total glycine and taurine derived from the bile acids, whilst the sulphur estimation gives the amount of taurocholic acid present. The value for glycocholic acid is then obtained by calculation. E. S.

Means for Differentiating between Chondrin and Glutin. M. A. RAKUZIN (*Chem. Ztg.*, 1923, **47**, 602).—Chondrin gives a very opalescent solution which gives the xanthoproteic reaction, whereas glutin gives a clear transparent solution in concentrations up to 0·75% which is not coloured by nitric acid. A hot 10% gelatin solution containing chondrin is immediately gelatinised by the addition of a saturated solution of chrome alum. A 0·2% chondrin solution shows no appreciable difference on addition of barium chloride owing to the already strong opalescence; if, however, the solution is stirred with 10% of aluminium hydroxide and filtered, the filtrate gives an immediate precipitate with barium chloride of the barium salt of chondroitinsulphonic acid ($[\alpha]_D = +46 \cdot 5°$). A gelatin solution gives an immediate precipitate with barium chloride.
A. R. P.

Preservative Principles of Hops. III. THOMAS KENNEDY WALKER (*J. Inst. Brewing*, 1923, **29**, 379—399; cf. this vol., i, 78).—Light petroleum does not appear to be a suitable solvent for the extraction of hops, as it is slow in its extractive action and, indeed, fails to extract the resins thoroughly in the cold, and is, moreover, liable to hasten the resinification of the β-acid. The author finds that extraction with methyl alcohol gives better results and a method is described for estimating the soft resins in hops by means of this solvent; the method gives higher results than those in common use. T. H. P.

Colorimetric Estimation of Hydrogen-ion Concentration in Soils. C. T. GIMINGHAM (*J. Agric. Sci.*, 1923, **13**, 69—73).—A difficulty in the estimation of hydrogen-ion concentration in soil extracts has been due to their turbidity. The author has used the displacement method of Parker (A., 1922, i, 511), whereby it is possible to obtain comparatively clear liquid suitable for colorimetric hydrogen-ion estimations. Comparison of the results with those obtained electrometrically shows a fair agreement. In some cases, however, the hydrogen-ion concentration estimated colorimetrically on the first, clear, portion of the percolate showed a less satisfactory agreement with the electrometric figure than that determined on the later, more turbid, portions. G. W. R.

Estimation of Humus in Soils. V. AGAFONOFF (*Compt. rend.*, 1923, **117**, 404—406).—A comparison of three methods of estimating the humus content of soils: (1) The ignition method, taken as giving standard results, (2) Simon's method (this vol., ii, 506), and (3) the sulphuric–chromic acid oxidation method. It was found that the second method gives practically the same results as method (1), whilst being much less tedious. Method (3) gives low results, which falls in line with Simon's work, and indicates that whilst all the humus substances in some soils are oxidised under the given conditions, in other soils only a portion of the humus is oxidised. The chlorine index of a soil gives a rough indication of its humus content. E. E. T.

General and Physical Chemistry.

Open-spark Spectra and their Application in Chemical Analysis. C. AUER VON WELSBACH (*Ann. Physik*, 1923, [iv], 71, 7—11).—The author advocates the more general application of spectrum analysis, and more especially the use of open-spark spectra in chemical analysis. Attention is directed to the change occurring in the spectrum of a substance due to the presence of other substances. J. S. G. T.

Grouping of the Lines in the Secondary Spectrum of Hydrogen. K. BASU (*Phil. Mag.*, 1923, [vi], 46, 417—420).—Objections to the application of the quantum relation $h\nu=W$ to the process of molecular dissociation underlying the emission of the secondary spectrum of hydrogen are briefly reviewed. Assuming that the lines in this spectrum originate in two hydrogen nuclei separated by a definite distance, with an electron revolving about them, an expression involving amongst other factors azimuthal and radial quantum numbers, and the intra-nuclear distance is derived for the frequencies of the emitted lines. Assuming the intra-nuclear distance to be 10^{-8} cm. the author shows that the calculated frequencies fall into five classes, and that within each class there is very close agreement between the calculated and observed values of the frequencies. J. S. G. T.

The Band-spectrum of Iodine. R. MECKE (*Ann. Physik*, 1923, [iv], 71, 104—134).—Particulars are given of measurements of 130 lines constituting the heads of bands in the absorption band-spectrum of iodine. These are classified into ten series and it is shown that the frequencies of respective lines in the various series can be represented by a formula of the Deslandres type expanded as far as n^3, namely, $\nu(n_1;\ n_2)=18320{\cdot}97-213{\cdot}76n_1+0{\cdot}596n_1^2+0{\cdot}0021n_1^3-80{\cdot}66n_2-1{\cdot}012n_2^2+0{\cdot}0033n_2^3$, the values of n_1 ranging from 0 to 9, and of n_2 from -33 to $+24$. Particulars of wave-lengths and frequencies are given for the constituent lines in the bands $\lambda\lambda$ 6781·89, 6877·36, 6837·32, and 6934·16 Å. The components may be represented by a Deslandres type of formula, thus: $\nu=\nu(n_1;\ n_2)-bm^2$, where the value of $2b$ deduced from measurements of one group of 50 lines is 0·0161, and from another is 0·0176, the value increasing with increase of the value of the parameter m. No evidence was obtained of the existence of P and R series of lines in the various bands. The relation of the resonance spectrum of iodine to its absorption spectrum is discussed. J. S. G. T.

The Effect of Metallic Surfaces on the Spectra of Mercury, Cadmium, Helium, and Oxygen. L. JANICKI and E. LAU (*Ann. Physik*, 1923, [iv], 7, 562—566).—Experiments carried out to ascertain the effect, if any, produced on the respective spectra of mercury, cadmium, helium, and oxygen excited in a discharge tube

by coating the constricted portion of the discharge tube with a semi-transparent layer of silver are described. In the case of the discharge in mercury vapour contained in such a tube, a mercury band-spectrum was strongly developed. In the case of the discharge in cadmium vapour, the band spectrum was more strongly developed in the silvered than in the unsilvered tube. A similar phenomenon was exhibited by the discharge in oxygen, the band spectrum being developed at a higher pressure in the silvered than in the unsilvered tube. Changes in the relative intensities of components of the line spectrum of mercury accompanied the development of the band spectrum in the vapour. No effect whatsoever was observed in the case of the discharge in helium. J. S. G. T.

Distribution of Intensity in, and Origin of the Band Spectrum of Nitrogen. H. Kirschbaum (*Ann. Physik*, 1923, [iv], **71**, 289—316).—Details are given of the variation with temperature of the intensities of lines in positive and negative groups of bands in the band spectrum of nitrogen, excited either in a canal-ray discharge or cathode ray discharge in the gas, the variation of temperature being effected either by external agency, or internally by electronic impacts at various gas pressures. The results indicate that the effects of high temperature in the positive column of the cathode discharge and of the impact of canal rays are the same, the respective intensities of the higher members of a band and the higher heads of bands in a group being in each case increased. It is concluded that either agency increases the amplitude of oscillation of the diatomic molecular systems originating the emission of the band spectrum. J. S. G. T.

The Band Spectrum of Carbon Monoxide. E. Hulthén (*Ann. Physik*, 1923, [iv], **71**, 41—49).—It is shown that the wave-lengths of the lines constituting the four bands λλ 5610, 5198, 4835, and 4393 Å. in the spectrum of carbon monoxide can be arranged in series, *P*, *Q*, and *R*, such that $R(m)-Q(m)=Q(m+1)-P(m+1)$, where the symbols have the customary significance. This relation is not quite so exactly satisfied by the band λ 4393 Å. as in the case of the other three bands. The relation $R(m)-Q(m)=3{\cdot}885\,m$ is found to hold for the bands λλ 5610, 5198, and 4835 Å., whilst for the remaining band, λ 4393 Å., the corresponding relation is $R(m)-Q(m)=3{\cdot}845\,m$. It is concluded that the three former bands originate in the same initial condition of the radiating molecule, whilst the bands λλ 4835 and 4393 Å. correspond with an identical final condition of the molecule. It is probable that the bands λλ 6622 and 6078 Å. belong to the system discussed. J. S. G. T.

Relation between the Spectra of Ionised Potassium and of Argon. P. Zeeman and H. W. J. Dik (*Ann. Physik*, 1923, [iv], **71**, 199—203).—The electronic configurations of the ionised potassium atom and of argon resemble one another in that each comprises eighteen electrons, and differ only in that the nuclear charge in the case of the former is one unit greater than in the

latter case. The displacement law of Kossel and Sommerfeld (A., 1919, ii, 378) indicates that the spark spectrum of any element is related to the arc spectrum of the preceding element in the periodic table. Literature dealing with the characteristic arc and spark spectra of potassium and of argon is briefly reviewed. It is remarked that the spark spectrum of singly ionised potassium is most readily excited by means of an electrodeless ring-discharge in potassium vapour. Paulson (A., 1915, ii, 194) showed that for lines in the argon spectrum included between λλ 9233 and 3319 Å. the respective frequencies can be expressed in terms of constants B, C, and D connected by the relations $B=A+846{\cdot}1$; $C=A+1649{\cdot}3$; $D=A+2256{\cdot}1$. The authors show that between the frequencies of lines included between λλ 6594 and 3063 Å. in the spark spectrum of potassium a similar and even simpler relation, expressed in the form $Q=P+847$; $R=P+1695$; $S=P+2542$, exists. The same numerical constant, approximately equal to 847, occurs in the expressions for A and Q, and the constant difference between succeeding members of the Q, R, S series is also equal to this constant. It is suggested that this constant has some simple physical significance. J. S. G. T.

Series of Multiple Lines with Fourfold Rydberg Constant in the Spectrum of Potassium. KNUD AAGE NISSEN (*Astrophys. J.*, 1923, **57**, 185—190).—Sixty-four lines between λ 1873 and λ 4608 have been arranged in one diffuse subordinate series, $(2p)-(md)$, and in sharp subordinate series, $(2p_x)-(ms')$, $(2p_y)-(ms'')$, $(2p_u)-(ms''')$, $(2p_s)-(ms')$, and $(2p_t)-(ms'')$. An average agreement within one unit is obtained between the observed values reduced to international vacuum wave-numbers and those computed by Ritz's formulæ. The results support Sommerfeld's suggestion that there is a relationship between the spark spectrum of an alkali and the arc spectrum of the inert gas with atomic number one less. (See also McLennan, A., 1921, ii, 667; Schillinger, *Sitzungsber. K. Akad. Wiss. Wien*, 1909, **118**, II, A, 266; A., 1910, ii, 369; Nelthorpe, *Astrophys. J.*, 1919, **41**, 16). A. A. E.

The Spark Spectrum of Rubidium. H. REINHEIMMER (*Ann. Physik*, 1923, [iv], **71**, 162—177).—Particulars are given of 142 lines included between λλ 3320 and 7320 Å. in the spark spectrum of rubidium excited in a discharge tube containing helium at about 3 mm. pressure, and of 12 lines in the arc spectrum of the metal. The displacement law of Sommerfeld and Kossel (A., 1919, ii, 378) indicates that if the spark spectrum of rubidium is attributable to the singly ionised atom of the metal, this spectrum should be analogous in structure to the arc spectrum of krypton. A direct comparison of these two spectra is at present impossible, but the comparison may be effected by way of the neon spectrum which is known to contain 10 p-terms. In this manner it has been found possible to classify 103 lines in the spark spectrum of rubidium into series containing a large number of p-terms. This result is held to confirm qualitatively the validity of the displacement law. J. S. G. T.

The Arc Spectrum of Lead. WALTER GROTRIAN (*Naturwiss.*, 1923, **11**, 255—256; from *Chem. Zentr.*, 1923, i, 1413—1414).—The absorption spectrum of lead at 700—800° shows a first line at 2823 Å., which is held to be due to the term corresponding with the normal lead atom. At 1100° lines occur at 3639, 3683, 4057, 2614, 2613, and 2577 Å. The line 2833 Å. is the fundamental line of a subsidiary series which occurs in emission as a transition from $2s$ to $2p_4$. G. W. R.

Spectrum Analysis of the Rare Earths. J. M. EDER (*Ann. Physik*, 1923, [iv,] **71**, 12—18).—The main characteristics of the arc spectra of the rare elements yttrium, erbium, thulium, lutecium, neo-ytterbium, samarium, gadolinium, europium, "eurosamarium," terbium, "welsium," and holmium are discussed. The author considers the elemental character of thulium and terbium to be definitely established. That of samarium is not certain. J. S. G. T.

The Spark Spectra of Aluminium. I and II. F. PASCHEN (*Ann. Physik*, 1923, [iv], **71**, 142—161; 537—561).—I. Particulars are given of the modes of excitation of the spectra of Al^{I}, Al^{II}, and Al^{III}. Various lines in the spark spectrum of doubly-ionised aluminium, Al^{III}, are classified into series and the spectrum is compared with those of Na^{I}, Mg^{II}, and H, the comparison confirming Bohr's conclusions relating to the electronic characteristics of these elements. In particular, it is pointed out that the ordinary spark spectrum of aluminium contains, in addition to a series of lines of the Fowler type, a series of lines analogous to those in the arc spectrum of Na^{I}, with the difference that Rydberg's constant, N, in the series-formula for the latter is replaced by $9N$ in the series-formula for the lines of Al^{III}, in accordance with Bohr's theory.

II. The author tabulates the intensities, wave-lengths, frequencies, and combination formulæ of about 300 lines in the spark spectrum of singly-ionised aluminium, Al^{II}. Various series of triplets in the spectrum are classified, and formulæ giving the frequencies of the series $4f_i-mf'$, $4p_i-ms$, mp_i-md_j deduced. Similarly, values of the respective wave-lengths, frequencies, and differences of frequencies of the systems of triplets in the spectrum of chlorine excited between aluminium electrodes in an atmosphere of helium containing very little chlorine are tabulated and discussed. The spark spectrum of Al^{II} is compared with those of Mg^{I} and hydrogen. J. S. G. T.

Regularities of the Spectral Lines of Iron and the Atomic Magnetic Field. H. NAGAOKA and Y. SUGIURA (*Nature*, 1923, **112**, 359).—A preliminary account of regularities observed, particularly between λ 2400 and λ 3000 Å. The results appear to support the magneton theory. It is thought that the intricate nature of the spectral lines in ferromagnetic metals may ultimately be traced to the existence of an inner atomic field. A. A. E.

Symmetrical Series of Lines in the Spectrum of Iron. A. HAGENBACH and H. SCHUMACHER (*Ann. Physik*, 1923, [iv], **71**, 19—40).—In continuation of previous work (*Arch. de Genève*, 1919, **1**, 231) the authors have found two pairs of symmetrical double series of lines, the symmetry relating to the frequencies of the lines in the spectrum of iron. The one pair of double series occurs towards the red end of the spectrum, the other towards the violet end. The centre of symmetry is very approximately the same for the respective members of each pair, thus for lines in the respective groups 1, 2, 3, and 4, the centres of symmetry occur at λλ 5135·395±0·151, 5132·943±0·174, 3683·04±0·14, 3682·05±0·12 Å. Formulæ involving three constants and a single variable parameter are deduced for the frequencies of the lines in the various groups. There are as follows: Group I, $\nu=194727\pm11412m^4/(m^2-1\cdot3544m+13\cdot581)^2$, $m=3, 4, 5 \ldots$; Group II, $\nu=194820\pm11743m^4/(m^2-0\cdot5038m+5\cdot7173)^2$, $m=2, 3, 4 \ldots$; Group III, $\nu=271515\pm6735m^4/(m^2-0\cdot384m+6\cdot48)^2$, $m=2, 3, 4 \ldots$; Group IV, $\nu=271588\pm6136m^4/(m^2-1\cdot20279m+10\cdot4354)^2$, $m=2, 3, 4 \ldots$. The effects of pressure and of a magnetic field (Zeeman effect) on the various groups of lines are briefly discussed. The symmetrical character of the wave-lengths of certain groups of lines discovered by Gehrcke in the spectrum of iron (A., 1921, ii, 612; *Physikal. Z.*, 1922, **23**, 432) is critically examined, and the author concludes that the data available are insufficient to decide whether such symmetry is best expressed in terms of wave-lengths or frequencies.

J. S. G. T.

Regularities in the Arc Spectrum of Vanadium. W. F. MEGGERS (*J. Washington Acad. Sci.*, 1923, **13**, 317—325).—Of the 2000 lines already measured in the arc spectrum of vanadium about 15% have been now assigned to multiplets, tables of sixteen of which are given. Vanadium as a representative of Group V of the periodic classification is thus shown to conform to the alternation law of Kossel and Sommerfeld, which is now verified for arc spectra across the entire table.

A. R. P.

Tesla-luminescence Spectra. III. Some Mono-substitution Products of Benzene. WILLIAM HAMILTON MCVICKER, JOSEPH KENNETH MARSH, and ALFRED WALTER STEWART (T., 1923, **123**, 2147—2163).

Absorption Spectra of Nitrosylsulphuric Acid and of the Complex Compounds of Copper Sulphate and Ferrous Sulphate with Nitric Oxide. H. I. SCHLESINGER and ALBERT SALATHE (*J. Amer. Chem. Soc.*, 1923, **45**, 1863—1878).—The absorption spectrum of nitrosylsulphuric acid dissolved in sulphuric acid of various concentrations has been obtained and examined. The spectra show that appreciable quantities of the former remain undecomposed when the sulphuric acid is diluted to 50% with water, and that in sulphuric acid of greater concentrations relatively large amounts of nitrosylsulphuric acid are present. This result disproves one of the fundamental assumptions made by Raschig in his development of the theory of the chamber process. Absorp-

tion spectra of the complexes formed by ferrous sulphate with nitric oxide in solutions of sulphuric acid of various concentrations have been photographed. The spectroscopic data confirm the view that there are two such complexes, both of the composition $FeSO_4,NO$, and show that one of them is stable when the concentration of the sulphuric acid is greater than 65%, and the other when the concentration of acid is below 50%. Absorption spectra of $CuSO_4,NO$ have also been obtained and the spectra of these complex salts have been compared with those of the so-called ferrous and cupric nitrosisulphonates and have been found to be identical. A preliminary investigation of the absorption spectrum of "nitrosisulphonic acid" has shown it to be very similar to that of the ferrous sulphate–nitric oxide complex existing in concentrated sulphuric acid solution. This result supports the view that possibly nitrosisulphonic acid should be regarded as an unstable solution of a complex compound of sulphuric acid and nitric oxide. Examination of the spectra of solutions of nitric acid in concentrated sulphuric acid, both before and after the solutions have been heated, shows that nitric acid is not readily decomposed in such solutions into nitrosylsulphuric acid, at least if the solution is not very concentrated with respect to nitric acid. The character of the absorption spectrum of nitrosylsulphuric acid favours the view that this substance is present in solution largely as nitrososulphonic acid. J. F. S.

The Spectrophotometric Method for the Investigation of Dyes in Textile Fabrics by Transmitted Light. N. USPENSKI and G. WORONKOV (*Z. Physik*, 1923, **17**, 112—116).—The application of the König-Martens polarisation spectrophotometer to the determination of the absorption curves of various dyes contained in various dyed textile fabrics—cotton, wool, and silk—is briefly described. J. S. G. T.

Phosphorescent Zinc Sulphide. A. A. GUNTZ (*Compt. rend.*, 1923, **177**, 479—482).—A study of the phosphorescence of mixed crystals of zinc and cadmium sulphides. The phosphorescence of zinc sulphide changes in colour from greenish-blue to red with increasing quantities of cadmium sulphide. With a 12%, 20%, and 30% content of the latter substance, the phosphorescence is, respectively, lemon-yellow, orange, and red. The orange phosphorescence induced by the addition of traces of manganese to zinc sulphide is neither vigorous nor persistent, whereas cadmium sulphide produces no effect unless present in fairly large quantities, and does not diminish the vigour or the duration of phosphorescence, the colour change being a light-absorption effect and not due to phosphorogenic action on the part of cadmium sulphide (cf. A., 1922, ii, 502). E. E. T.

Chemical Constitution and Rotatory Power. VI. Influence of the Chemical Function of the Substituent Groups. MARIO BETTI (*Gazzetta*, 1923, **53**, i, 417—431).—The results previously obtained (A., 1907, ii, 661, 726; 1916, ii, 279; 1921, i, 107) are summarised. T. H. P.

Partial and Consecutive Reactions in the Photosensitive System: Quinine Sulphate, Chromic and Sulphuric Acids. GEORGE S. FORBES, JOHN C. WOODHOUSE, and REGINALD S. DEAN (*J. Amer. Chem. Soc.*, 1923, **45**, 1891—1895).—The photochemical oxidation of quinine sulphate by chromic acid in the presence of sulphuric acid in the light emitted by a quartz mercury lamp has been investigated. With two photochemically activated reactants the total reaction velocity should be the sum of four partial reactions with four different velocity constants. One involves two activated molecular species, another only unactivated species, and two others involve one activated and one unactivated species. It is shown from the present work that species known to be activated in some reactions may give no evidence of activation in others. The concentration of a photochemically unactivated reactant is shown to be without effect on the velocity of a photochemical reaction, provided that its concentration is not so small that its reaction with activated reactants does not become the slow stage of the total process. J. F. S.

Long-range Particles from Radium-active Deposit. GERHARD KIRSCH and HANS PETTERSSON (*Nature*, 1923, **112**, 394—395).—By enclosing dry radium emanation mixed with oxygen in thin-walled capillaries of potassium glass or silica lined with aluminium foil (thickness 12 μ) pressing well against the glass, a strong and practically constant source of hydrogen nuclei is obtained. This method has been applied to scandium, vanadium, and cobalt (as oxides), arsenic, and indium (as chlorides); these elements do not give off long-range particles (>30 cm. of air) in greater number than $3\times$ or $4\times N . 10^{-8}$, where N is the number of α-particles from radium-C discharged within the capillary.

By spreading substances over copper foil (which, after removal of occluded gases, showed a comparatively small number of hydrogen particles, probably "neutral" particles), fairly conclusive evidence was obtained that hydrogen nuclei are emitted from silicon, glucinum (oxide), magnesium (oxide), and lithium (carbonate), the approximate maximal ranges in air being, respectively, 12 cm., 18 cm., 13 cm., and 10 cm. A. A. E.

The β-Ray Spectrum of Uranium-X_1 and its Significance. LISE MEITNER (*Z. Physik*, 1923, **17**, 54—66).—The β-ray magnetic spectrum of uranium-X_1 has been found to consist of three sharp lines corresponding, respectively, with values of $H\rho$ equal to 1057, 1028, and 927, and a faint band the centre of which corresponds with a value of $H\rho$ equal to 1163, H denoting the strength of the magnetic field employed measured in Gauss units, and ρ the radius of curvature (in cm.) of the respective paths of the emitted β-rays in the field. The three sharp lines originate in the L, M, and N levels and the corresponding rays are ejected by the K_α characteristic radiation of the thorium isotope uranium-X_1 excited by the primary β-rays. Individual atoms are concerned throughout the whole process of disintegration. Apart from characteristic Röntgen radiation, no γ-rays are emitted by uranium-X_1. The

results indicate that the primary β-rays are emitted from the atomic nucleus with a definite velocity, and are in agreement with the suggestion of Rosseland (*Z. Physik*, 1923, **14**, 173) that an excited atomic system can pass to the unexcited state by the emission of one of its constituent particles in the form of a corpuscular ray as an alternative to the emission of radiation. J. S. G. T.

The γ-Rays of Uranium-X and their Relation to Uranium-X_1 and Uranium-X_2. OTTO HAHN and LISE MEITNER (*Z. Physik*, 1923, **7**, 157—167).—In continuation of previous work (preceding abstract), the authors have determined the absorption, by various thicknesses of lead, of the γ-rays emitted by uranium-X, and the distribution of the respective groups of rays amongst the components uranium-X_1 and uranium-X_2. The experimental method employed eliminated the effect of β-rays from the observations. Three classes of rays were distinguished in the radiation emitted from uranium-X, and these were characterised by the following respective values of the thickness of lead required to reduce their initial activities by one-half: 9·6, 3·0, and 0·36 mm. Taken in conjunction with the results of Richardson (A., 1914, ii, 160) the results indicate that four types of γ-rays are emitted by a mixture of uranium-X_1 and uranium-X_2. Of these, the nuclear hard γ-rays (9·6 mm., 3·0 mm.) are associated with uranium-X_2 entirely, whilst the remaining group of γ-rays observed (0·36 mm.) and that observed by Richardson (half-absorption value 0·29 mm. aluminium) are associated entirely with uranium-X_1 and constitute, respectively, the characteristic K- and L-Röntgen radiation, a conclusion which is in agreement with a deduction drawn by Meitner from previous work concerned with the analysis of the β-radiation emitted by uranium-X (*loc. cit.*). J. S. G. T.

Electrochemistry of Gases. S. C. LIND (*Amer. Electrochem. Soc.* [advance copy], 1923, 61—69).—A theoretical paper in which as a result of kinetic studies of gas reactions under ionising conditions (α-radiation), the following new principles, which are supported by recent electronic evidence may be put forward. Gaseous ions tend to form additive products with neutral molecules, which complexes are the intermediate products of gaseous electrochemical reactions. As a deduction from the above, ions do not interact, nor do molecules or atoms otherwise activated interact. Their momentary concentrations are too low; they react only with neutral or unactivated molecules. A low momentary concentration of an activated substance is capable of explaining the action of negative catalysts or inhibitors. Active ions may be destroyed by reverse action either in a uni- or multi-component system, without any effective chemical action resulting. This reversal may be prevented by a suitable acceptor. Free electrons will play a primary part in producing chemical reaction only in gaseous systems containing at least one gas with affinity for electrons. Absence of such a gas will result in a reaction with a lower M/N ratio than when one is present. A secondary rôle is always played by electrons in restoring final electrical neutrality. J. F. S.

Electricity in Flames. H. A. Wilson (*Amer. Electrochem. Soc.* [advance copy], 1923, 51—60).—A theoretical paper in which the present state of knowledge on the electrical properties of flames is reviewed. The electrical conductivity of salt vapours in flames, ionic mobilities in flames, the behaviour of flames in a magnetic field, the charge carried by the ions of salt vapours at high temperatures, the electrical conductivity of flames for rapidly alternating currents, and the thermodynamical theory of ionisation at high temperatures are considered. A bibliography of the subject is appended to the paper. J. F. S.

The Quinhydrone Electrode as a Comparison Electrode. Stig Veibel (T., 1923, **123**, 2203—2207).

Oxidation-Reduction. W. Mansfield Clark (*U.S. Pub. Health Rep.*, No. 823).—A theoretical treatment of oxidation, involving the measurement of oxidation potentials. J. F. S.

Heat Losses and Chemical Action in the High-voltage, High-frequency Discharge through Air. Farrington Daniels, Paul Keene, and P. D. V. Manning (*Amer. Electrochem. Soc.*, 1923, 141—151. [Advance copy]).—Experiments with a high frequency corona discharge at about 100,000 volts indicate that of the energy supplied to the discharge chamber, about 2% only was converted into chemical energy. This chemical efficiency is of the same order as that afforded by arc and other types of corona discharges in air. Short exposures to the discharge gave higher chemical efficiencies than long ones. The ratio of ozone to nitric acid produced by the discharge varied from 2·4 to 16, according to the character of the discharge, an increase of nitric acid accompanying an increase of intensity of the pink streamers, whilst uniformity of the blue corona increased the proportion of ozone. J. S. G. T.

Source of Trouble in Electrometric Measurements of Hydrogen-ion Concentration. W. T. Bovie and Walter S. Hughes (*J. Amer. Chem. Soc.*, 1923, **45**, 1904—1905).—It is pointed out that inaccuracies in the measurement of hydrogen-ion concentration may arise, which are due to the diffusion of mercuric chloride from the calomel electrode. This substance poisons the hydrogen electrode, slightly at first, but more as time goes on until eventually no trustworthy measurements can be made even with freshly platinised electrodes. A method of avoiding this error is described which can be used with a quadrant electrometer, which consists in closing the mouth of the calomel electrode with a very thin-walled glass bulb which is inserted in the liquid and is sufficiently conducting when an electrometer is used but not when a galvanometer is employed. J. F. S.

A Comparison of the Heating-curve and Quenching Methods of Melting-point Determinations. George W. Morey (*J. Washington Acad. Sci.*, 1923, **13**, 326—329).—Comparison of the results obtained with sodium metasilicate shows that the melting

point determined by the heating-curve method is about 2° lower than that obtained by the quenching method, which is probably the more correct. The latter point lies on the sharply rising section of the heating curve just after the section that is flattened out. [Cf. *J.S.C.I.*, 1923, Oct.] A. R. P.

The Calorific Value of Carbon Compounds. DIMITRI KONOVALOV (T., 1923, **123**, 2184—2202).

The Density of Liquids below 0°. JEAN TIMMERMANS (*Bull. Soc. chim. Belg.*, 1923, **32**, 299—306; cf. A., 1912, ii, 738).—The densities between 0° and the freezing points of ammonia, phosphorus trichloride, carbon disulphide, ethyl bromide, propionitrile, ethyl alcohol, and *n*-propyl alcohol are determined. It is shown that the scale of low temperatures adopted by the French is identical with that adopted in America, but is different from the German. The rule previously enunciated, $d_{\text{max.}}/d_{\text{crit.}}=d_{\text{crit.}}/d_{\text{theor.}}$, is confirmed. H. H.

Metallic Cementation. H. WEISS (*Ann. Chim.*, 1923, [ix], **19**, 201—275).—The author has studied the interfacial penetration of copper with nine other metals under various conditions, and, although the results show considerable variation both with temperature and with the nature of the second metal, he was able to draw certain general conclusions as to the nature and mechanism of the action. [Cf. *J.S.C.I.*, 1923, 982A.] H. J. E.

Equilibrium of the Ternary System Bismuth–Tin–Zinc. SHEIKH D. MUZAFFAR (T., 1923, **123**, 2341—2352).

The Kinetics of the Reaction between Ferrous Phosphate and Sulphur Dioxide in Phosphoric Acid Solution. SYDNEY RAYMOND CARTER and JOHN ALFRED VALENTINE BUTLER (T., 1923, **123**, 2370—2380).

Inversion of Sucrose by Saccharase. H. VON EULER and K. MYRBÄCK (*Z. physiol. Chem.*, 1923, **129**, 100—105).—The inversion of sucrose by purified saccharase is approximately unimolecular (cf. Kuhn, this vol., i, 401), the reaction constant at optimum p_H showing only a very slight increase with time. Michaelis's constant, $k_M=[23\cdot75\log(R+L)/(D+L)+32\times0\cdot305(R-D)/(R+D)]/t$, remains very constant both for purified saccharase and for crude yeast extract. W. O. K.

Influence of Neutral Salts on the Temperature Coefficient of Reaction Velocity. F. O. RICE and WILLIAM LEMKIN (*J. Amer. Chem. Soc.*, 1923, **45**, 1896—1900).—The velocity of the reaction between iodine and acetone in the presence of nitric, hydrochloric, hydriodic, perchloric, benzenesulphonic, trichloroacetic and naphthalene-2-sulphonic acids and also in the presence of normal salts of sodium, potassium, rubidium, lithium, and magnesium has been determined at 25° and 23°, and the temperature coefficient calculated for each case. It is shown that the temperature coefficient is the same for all strong acids, and it is unaffected

by the presence of salts of the acid. The reaction has a lower temperature coefficient when catalysed by weak acids. If the acids are arranged in descending order of their strengths, this is also the order of diminishing temperature coefficients. When the reaction is catalysed by sulphuric acid, the presence of one of its salts diminishes the temperature coefficient considerably. This is probably true for all weak acids. Small quantities of about $0.01M$ of salts of the alkali metals increase the velocity slightly. There is no indication of any diminution such as might be expected on the basis of the law of mass action. J. F. S.

Line Spectra and Atomic Structure. NIELS BOHR (*Ann. Physik*, 1923, [iv], **71**, 228—288).—The quantum theory of the origin of spectral series, developed by the author, and the relation of spectra to atomic structure are reviewed. J. S. G. T.

An Explanation of the Theory of the Rotation of the Atomic Nucleus. III. HERBERT HENSTOCK (*Chem. News*, 1923, **127**, 18—21).—The author's theory (cf. this vol., ii, 477) is applied to the consideration of the structure of the oxides of the elements of groups I to IV of the periodic system. A double bond between a bivalent metal and oxygen may be formed by the juxtaposition of the faces of the respective cubic octets, the two nuclei being orientated perpendicularly to one another. In certain cases, for instance carbon monoxide, it is necessary to assume distortion of the octet. If the uncombined carbon atom has a tetrahedral form, in carbon monoxide it may have a semi-cubic, semi-tetrahedral form. The absence of free lines of force in the combined carbon atom will then account for the stability of the compound. A distorted octet must be characteristic of those atoms which have few electrons in their outer layers. E. H. R.

Structure of the Molecule. A. PEARSE JENKIN (*Nature*, 1923, **112**, 326).—The suggestion that both dynamic and static electrons take part in the formation of the molecule is applied to the cases of water and tartaric acid. A. A. E.

A Static Model of the Hydrogen Molecule. H. STANLEY ALLEN (*Proc. Roy. Soc. Edin.*, 1922—1923, **43**, 180—196).—A model of the hydrogen molecule, based on the assumption of the existence of the "quantum force," $n^2h^2/4\pi^2mr^3$, postulated by Langmuir (*Physical Rev.*, 1921, **18**, 104), varying inversely as the cube of the distance, and of which the sign depends on the signs of the electrical charges involved, is described. The model possesses many of the properties of the Bohr model of the hydrogen molecule, with the important difference that the electrons are at rest relatively to the hydrogen nuclei. Of the various possible electronic equilibrium configurations, the most stable is that in which the nuclei and electrons are situated at the corners of a square, the nuclei being at the extremities of one diagonal and the electrons at the ends of the other. The length of the diagonal is 0·871 Å. and the moment of inertia of the molecule $6{\cdot}261\times10^{-41}$ c.g.s. unit. The work necessary for the complete disintegration

of the molecule corresponds with a potential difference of 30·06 volts. In the case of the charged hydrogen molecule with only one electron, the distance between the nuclei is 1·239 Å., and the ionisation potential 17·34 volts. Calculated and experimental values of the ionisation potentials are in moderately good agreement. A possible configuration for the molecule of triatomic hydrogen (Thomson, "Rays of Positive Electricity," 1921, 196), in which nuclei and electrons are disposed at alternate corners of a regular hexagon, is suggested. It is pointed out that a static model of the hydrogen molecule accords with the diamagnetic character of the element and with evidence derived from band spectra.

J. S. G. T.

The Curves of the Periodic Law. W. M. THORNTON (*Phil. Mag.*, 1923, [vi], **46**, 442—448).—The minor fluctuations exhibited by the graph associated with the presentation of the periodic law, in which the densities of the elements are plotted as ordinates against the respective values of the atomic weights as abscissæ, are discussed. It is shown that the main features of the curve can be represented by a fundamental wave-form in which the amplitude and period vary; it represents the periodic change in the configuration of the outer electrons in an atom under their own forces. Superposed on this fundamental, in order to reproduce the minor fluctuations, is, after the manner employed in harmonic analysis, a smaller wave-form of double the frequency of the fundamental, the amplitude and phase of this second wave-form being chosen by inspection. It is shown that the physical and chemical properties of the elements appear to depend as much on the minor periodicity as on the fundamental. This is exhibited by a series of curves in which ordinates represent the densities of the respective elements and abscissæ represent the projections of the major harmonic curve, referred to, on the vertical axis. Properties of the elements —density, radioactivity, stability, contraction, and expansion, ductility—are discussed in connexion with these curves.

J. S. G. T.

Nature of Chemical Valency. W. NERNST (*Z. angew. Chem.*, 1923, **36**, 453—455).—The hydrogen atom is the only chemical substance of the structure of which we have up to the present obtained a satisfactory and definite picture, because only in this case, that of two electrically charged units of mass, are the quantum energy relationships understood. Pauli's conception of the hydrogen molecule (A., 1922, ii, 703) as two hydrogen nuclei which may be considered as relatively at rest, around which a free electron vibrates round the surface of an ellipsoid of rotation, is considered to be a conception of the nature of valency capable of extension to all chemical compounds, although, of course, our knowledge does not enable us to supply the details in other cases. The conception is extended to the case of the theoretically simplest crystalline structure—that of hydrogen atoms—and the resultant forces exerted by the vibrating electrons are shown to be equivalent to

six subsidiary valencies arranged in space at right angles to one another. These valencies would not, however, exercise a continuous but a pulsating force, causing the positive nuclei to undergo vibrations of very small amplitude with relation to one another, even at the absolute zero of temperature. The same conception can be applied to the molecules in potassium chloride vapour, the molecule being held together by a free electron belonging to the potassium atom, travelling in an ellipsoidal path round the potassium and chlorine atoms. The distinction between polar and non-polar valency is considered to be determined by the behaviour of the free electron when the compound is decomposed. In the case of polar or dualistic compounds, the electron passes on decomposition to the other atom of the former compound and ionisation is the result. Ordinary crystals are cases of non-polar valency, the binding electrons remaining with their original partners on dissolution of partnership. Whether ionisation occurs or not will depend on the structure of the constellation of electrons associated with the atoms in question. These considerations apply only to matter in the neighbourhood of absolute zero of temperature. At higher temperatures, the matter is complicated by the superposition of heat vibrations on the simple vibrations here considered. The conception is also applicable to the conductivity of electricity through metals. H. C. R.

Studies of Electrovalency. II. Co-ordinated Hydrogen. Thomas Martin Lowry and Henry Burgess (T., 1923, **123**, 2111—2124).

The Relationship of the Tautomeric Hydrogen Theory to the Theory of Induced Alternate Polarities. Fred Allsop and James Kenner (T., 1923, **123**, 2296—2315).

Chelate Co-ordination. J. D. Main Smith (*Chemistry and Industry*, 1923, **42**, 847—850).—A criticism of Lowry's views (this vol., ii, 555) that two types of co-ordination exist, centric and cyclic; these two terms are not mutually exclusive, for all cyclic groups have centric atoms at their reacting ends. There is no need to modify the term "chelate group" until it has been proved that fundamentally different types of co-ordination exist. Lowry's criticism merely directs attention afresh to the fact, insisted on by Werner, that differences in stability in co-ordination compounds are due to differences in intensity, but not in type, of co-ordination. Against Lowry's view that ethylenediamine should not be regarded as a chelate group, evidence is quoted to show that it is, on the contrary, a chelate group of maximum activity. Morgan's idea of a chelate group is defined precisely as "a linked system of atoms which, in combination with another atom, completes a cyclic system." The resolution of the ferrous αα-dipyridyl complex is quoted as evidence against Lowry's statement that ring formation does not directly promote co-ordination, and the fact that αα-diquinolyl does not form co-ordinated ferrous compounds

contradicts Lowry's general conclusion that the maximum of stability should be reached in a six-atom ring containing three pairs of conjugated atoms. The fact that no compounds, stable or unstable, are found in the case of αα-diquinolyl is proof that conjugation external to the chelate group is not even a minor factor in co-ordination. All co-ordination compounds are held to be of the same ("centric") type. F. A. M.

Electron Theory of Chemistry. Changes in Chemical Properties produced by the Substitution of One Element by Another, with Applications to Benzene Substitutions. (SIR) J. J. THOMSON (*Phil. Mag.*, 1923, [vi], 46, 497—514).—The author investigates the nature of the change in and around the molecule, and the effect produced on the chemical properties of the molecule, by the substitution of a univalent atom or radicle for an atom of hydrogen whereby the number of electrons in the molecule is increased. It is shown that the electrical effect of such substitution may be represented by the introduction of an electric doublet at the hydrogen atom. The sign of the doublet depends on the nature of the radicle. In the case of radicles of type I, including Cl, Br, I, OH, NH_2, CH_3, each containing 7 electrons forming an uncompleted octet, the positive end of the doublet will be directed towards the molecule with which the hydrogen is combined and its negative end away from it. In the case of the substitution of hydrogen by radicles of type II, including O:N:O, OH·C:O, H·C:O, and CN, each containing one electron in excess of the number required to form complete octets, the doublet will be directed in the opposite direction to that characterising type I. The magnitude of the electrostatic moment introduced by the respective substitutions indicates that, in agreement with experimental results, the specific inductive capacities of water, and methyl, ethyl, and propyl alcohols, referred to the same number of molecules in the liquid state, should be approximately equal. Immediate deductions from the natures of the electric field produced by the two types of substitutions referred to include the following. Where one carbon atom in a carbon compound has been halogenated, it is more likely to be still further halogenated than a carbon atom associated with hydrogen atoms none of which have been replaced by halogen atoms. The same rule applies to the process of oxidation of an organic compound. The substitution of hydrogen by atoms and radicles of type I, *e.g.*, the substitution of two hydrogen atoms in methyl alcohol to form formic acid, should increase the acidity of the compound. This is further illustrated by the relative acidities of mono-, di-, and tri-chloroacetic acids, where, however, a further factor involving the period of existence of the acid in one or other of two phases is probably concerned. In the case of carbon atoms connected, as in ethylene, by a double bond, the substitution of a hydrogen atom by an atom of chlorine, etc., results in polarisation of the double bond. It follows that additive compounds would be more freely formed with a compound such as CH_2:CHCl than with one like CH_2:CH_2.

In the case of a series of carbon atoms occupying positions designated in succession, starting from one end of the chain, by the numbers 1, 2, 3, 4, 5 . . ., when the substituent atom or radicle is of type I, the active carbons are those which are 1, 3, 5 . . . places from the atom where substitution took place, whilst when the substituent is of type II, the active carbon atoms are 2, 4, 6 . . . places away from the substituent. This is illustrated by the case of substitution of hydrogen in benzene. Substituents which direct a second substituent into the ortho- and para-positions include Cl, Br, I, OH, NH_2, and CH_3 (type I), whilst NO_2, CO, OH, CN, HSO_3 (type II), as substituents, direct a second substituent into the meta-positions. The high values of the respective specific inductive capacities of benzonitrile, nitrobenzene, and phenylacetonitrile are in accord with deductions from the theory. In the case of di-substituted benzenes, if both substituents belong to the same type, the specific inductive capacity will be least for the para- and greatest for the ortho-substitution, the value for the meta-substitution being unchanged. If the two substituents belong to different types, the specific inductive capacity will be greatest for the para- and least for the ortho-substitution. The author suggests that determinations of specific inductive capacities of di-substituted bodies might thus be employed in determining whether the second substituent enters into the ortho-, meta-, or para-position. J. S. G. T.

The Geber Question. J. Ruska (*Chem. Ztg.*, 1923, **47**, 717—718).—Observations by an orientalist contributing to the study of works ascribed to Geber (cf. Darmstaedter, this vol., ii, 628). A. A. E.

The Works of Geber. J. R. Partington (*Chemistry and Industry*, 1923, **42**, 790—791).—Polemical against Lippmann (this vol., ii, 314; see also Partington, this vol., ii, 148, and Darmstaedter, this vol., ii, 628). A. A. E.

Concerning Geber. Ch. M. Van Deventer (*Chem. Weekblad*, 1923, **20**, 514—515).—In view of the work of Holmyard and of Partington (this vol., ii, 148) the author withdraws his view that Geber wished to pass as an older and more famous Dschâbir, but suggests the former name may have been a pseudonym of a writer of the early fourteenth century. S. I. L.

Extraction Apparatus for Large Amounts of Liquids. Hartwig Franzen (*Z. physiol. Chem.*, 1923, **129**, 307—308).—An electrically driven and electrically heated apparatus, which can be run continuously for months, and may have a capacity of more than 25 litres, is described with the aid of a diagram. W. O. K.

Inorganic Chemistry.

Chemical Action and the Disappearance of Gas in the Electrical Discharge Tube. F. H. NEWMAN (*Amer. Electrochem. Soc.* [advance copy], 1923, 43—49).—Hydrogen and nitrogen are absorbed in the presence of different elements, deposited on the walls of the cathode of a discharge tube, when the discharge is passing. The elements which exhibit this effect most strongly are phosphorus, sulphur, iodine, sodium, potassium, and the alloys of sodium and potassium. The rate of disappearance of the gas is greatest with phosphorus, sulphur, and iodine, and the final pressure attained is a minimum with phosphorus and sulphur. There is a similar absorption of these two gases when they are ionised by α-rays from polonium. The disappearance of the gas is due to the production of chemical compounds (nitrides and hydrides). The formation in this manner of nitrides of sodium, potassium, magnesium, and tin, and the hydrides of sodium, potassium, and sulphur have been proved by chemical analysis of the products. The gas under the ionising effect becomes modified, assuming an active condition which consists probably of triatomic molecules.

J. F. S.

The Photochemical Decomposition of Chlorine Monoxide. EDMUND JOHN BOWEN (T., 1923, **123**, 2328—2330).

Reaction between Bromine and Ammonium Salts and its Effect on the Precipitation of Manganese Dioxide. STEPHEN G. SIMPSON (*J. Amer. Chem. Soc.*, 1923, **45**, 1883—1890).—The effect of the presence of ammonium salts on the precipitation of manganese dioxide by bromine water following a basic acetate separation has been investigated, by determining the amounts of bromine used up in reactions with solutions of (*a*) ammonium sulphate, (*b*) manganous sulphate, (*c*) mixtures of the two, under varying degrees of initial acidity and in the presence of varying amounts of alkali acetate. The results show that each of the reactions is progressively retarded by an increase in the initial concentration of acid, and progressively accelerated by an increase in the concentration of acetate present, and the effect is greater in the case of the manganese salt than in the corresponding case of the ammonium salt. In the absence of acid, ammonium-ion and manganous-ion are quantitatively oxidised by bromine water, but the amount of free bromine used up is slightly in excess of the amount theoretically necessary. The results can be explained by considering the mass-action effect of the hydrogen-ion and of the acetate-ion on the equilibrium reaction between bromine and water, and assuming that the hypobromous acid formed oxidises the ammonium-ion and the manganous-ion more readily than does bromine and under existing conditions also decomposes slightly into oxygen and bromine. When ammonium and manganous salts

are present together in neutral solution in the presence of acetate, the ammonium-ion is more readily oxidised by bromine water, and by its formation of hydrogen-ions retards the precipitation of manganese dioxide. J. F. S.

Thunderstorms and Ozone. WILLIAM C. REYNOLDS (*Nature*, 1923, **112**, 397).—Analyses of atmospheric air showed that there was no appreciable increase of the nitrogen peroxide content of the air during or after a thunderstorm, whilst the quantity of ozone was increased by two to seven times. A. A. E.

The Ternary System, Sulphur–Selenium–Tellurium. L. LOSANA (*Gazzetta*, 1923, **53**, i, 396—410).—The author summarises and supplements previous results obtained with the three binary systems included in the ternary system sulphur–selenium–tellurium, and gives the results of his own thermal, dilatometric, and micrographic investigations of the ternary system.

In the case of sulphur–selenium, Ringer (A., 1902, ii, 651) has shown that there is complete miscibility in the liquid, and partial solution in the solid, state, and that the compound Se_2S possibly exists within certain limits of temperature. For selenium–tellurium Pellini and Vio (A., 1906, ii, 663) found formation of mixed crystals, with no miscibility gap, throughout the whole extent of the system, so that the two component elements are isomorphous.

For sulphur–tellurium some disparity exists between the results of different investigators. The author's thermal measurements confirm the value, 1·9%, of tellurium given by Pellini (A., 1909, ii, 726, 805) to the limit of complete miscibility, and show that the minimum on the liquid curve is about 6% of tellurium, with which the maximum eutectic arrest corresponds. With more than 97·6% of tellurium there is no trace of arrest and the end of the solidification is perceptible with moderate clearness; Chikashigé's statement that mixed crystals are formed with 98—100% of tellurium (A., 1911, ii, 978) is thus confirmed. In its middle portion the curve agrees generally with the results of Chikashigé and, especially, of Pellini.

The ternary system exhibits formation of neither compounds nor ternary eutectics, but contains two zones of complete miscibility in which there exist mixed crystals of selenium and tellurium in sulphur and mixed crystals of sulphur and tellurium in selenium. The formation of mixed sulphur–tellurium crystals is favoured by the presence of selenium, which causes solid solutions with high proportions of tellurium to be formed; many of such solid solutions exhibit, however, the phenomenon of more or less rapid de-mixing. The first transformation point of sulphur is depressed considerably by selenium and tellurium separately and to a still greater extent by the two elements together. T. H. P.

Production of Nitrogen Oxides and Ozone by High Voltage Electric Discharges. KARL B. MCEACHRON (*Amer. Electrochem. Soc.* [advance copy], 1923, 71—86).—The production of nitric oxide and ozone in tubes of various designs under various

pressures and electrical conditions has been investigated. It is shown that the previous electrical history of the gas has a marked effect on the character of the discharge and the products formed. Traces of the products of previous experiments, made in small tubes of the Siemens type, modify the character of the discharge and decrease the absorbable products. Increase of current flowing in the discharge increases the yield of both ozone and nitric acid up to a certain maximum, beyond which further increase in current decreases the yields. With increase of pressure, the yields of ozone increase until a pressure near to that of the atmosphere is reached. At higher pressures, the yields in general decrease. With decreasing pressures, within the limits investigated, the yield of nitric acid increases with tubes in which sparking occurs, and decreases in tubes, like the rod tubes, in which sparking does not occur. Increase in the rate of air flow will in general increase the yields of nitric acid up to a certain maximum, the critical air flow rate being dependent on the tube used. Increased air rates give increased yields of ozone which tend to become constant at higher rates. Sparks passing through air cause a pressure increase much too rapid to be a heat effect. With an enclosed volume of air, a pressure decrease occurs at the instant the power is disconnected, which is the pressure change due to ionisation noted by Farwell. A tube of the rod type, if properly cooled, gives yields of ozone of sufficient magnitude, so that the tube becomes of importance as a commercial ozoniser. In air, the corona discharge favours the production of ozone, whilst sparks tend to produce oxides of nitrogen. Some exceptions may be found to this, as in Siemens tubes, where the yield of nitrogen pentoxide was at times quite large, and yet the discharge consisted of a fine glow only. A combination of sparks and corona produces the higher oxides which are desirable from the absorption point of view. J. F. S.

The Slow Oxidation of Phosphorus. ELIZABETH GILCHRIST (*Proc. Roy. Soc. Edin.*, 1922—1923, **43**, 197—215).—Visible glow is emitted from phosphorus during oxidation only when the action occurs at a certain minimum rate, and is probably attributable to the oxidation of phosphorus trioxide, which must occur at a considerably slower rate than the oxidation of phosphorus to phosphorus trioxide preceding this action. The glow occurs chiefly in the gas phase, and may be steady, fluctuating, or intermittent. The rate of the reaction increases with rise of temperature, and at partial pressures of oxygen of about one atmosphere the rate is diminished with increase of oxygen pressure and may be slowed below the glowing point. The presence of ozone in oxygen greatly increases the glow, but the glow is not under ordinary conditions attributable to ozone produced in the reaction. A trace of moisture seems necessary to start the reaction, but as the pressure of water vapour increases, the rate attains a maximum value and thereafter falls. Gases and vapours capable of developing negatively-charged carbon molecules, *e.g.*, ethylene, acetylene, or ethane, are negative catalysts towards the reaction, whilst others,

including ammonia and methyl alcohol, are promoters of the reaction. J. S. G. T.

The Reaction between Phosphorous Acid and Iodine. ALEC DUNCAN MITCHELL (T., 1923, **123**, 2241—2254).

Action of Potassium Carbonate on Lead Glass. H. DROOP RICHMOND (*Analyst*, 1923, **48**, 260—262).—When stored in lead glass bottles, potassium carbonate may become contaminated with considerable quantities of lead and arsenic derived from the glass. This action of the salt on the glass is relatively rapid if moisture is admitted to the bottle owing to a defective stopper. W. P. S.

Correction to the Freezing-point Diagram of Lead-Sodium Alloys. G. CALINGAERT and W. J. BOESCH (*J. Amer. Chem. Soc.*, 1923, **45**, 1901—1904).—The thermal data obtained by the authors for lead-sodium alloys (6[illegible] atomic % of sodium) differed appreciably from Mathewson's results (A., 1906, ii, 666); consequently they have determined the freezing-point data for alloys between 50 and 75 atomic % of sodium. It is shown that the pure compound separating from alloys of lead and sodium, the composition of which is between 58·8 and 76·6 atomic % of sodium, is Na_5Pb_2, this compound forming solid solutions with both NaPb and Na_4Pb. Alloys containing 58·8 to 71·4 atomic % of sodium rearrange at 182° on cooling, the compound Na_5Pb_2 disappears and a new compound, Na_2Pb, is formed. The complete diagram of lead-sodium alloys is given corrected for the above results. J. F. S.

The Crystal Structure of Sodium Chlorate. WILHELM KIBY (*Z. Physik*, 1923, **7**, 213—250).—The work of Kolkmeijer, Bijvoet, and Karssen (A., 1921, ii, 200) and of Dickinson and Goodhue (A., 1922, ii, 145) on the determination of the crystal structure of sodium chlorate by Bragg's method of *X*-ray crystal analysis is briefly reviewed. Wulff (*Z. Kryst.*, 1922, **57**, 190) employing Laue's method of analysis, calculated values of the parameters differing considerably from those found by the previous observers. The present paper contains the mathematical analysis of a method whereby the crystallographic parameters of a crystal of sodium chlorate are determined from a consideration of the distribution of intensities in the *X*-radiation diffracted in various directions by the crystal, as evidenced by the intensities of the photographic point images contained in the appropriate Laue *X*-ray diagram. In the case of a crystal of sodium chlorate, such a diagram contains 51 points in each quadrant. Employing the method of combination suggested by Schiebold, sixteen only of these points are required in the analysis. The following assumptions amongst others are made in the analysis: that the structure is close-packed; the oxygen atoms in the crystal structure lie each in contact with the appropriate chlorine atom and the two nearest sodium atoms and each lies in the plane defined by these three atoms; each chlorine atom is at an equal distance from each of the corresponding two sodium atoms referred to. With these assumptions, it is shown that the values of the parameters *a*, *b*, *p*, *q*, and *r* referring, respect-

ively, to the co-ordinates of a sodium atom, a chlorine atom, and the three oxygen atoms in a molecule of sodium chlorate, which enable the positions of all atoms within the structure to be calculated are *a*, 0·071; *b*, 0·429; *p*, 0·301; *q*, 0·473; *r*, 0·590. The values are in close agreement with those deduced from the work of Dickinson and Goodhue referred to. J. S. G. T.

The Properties of Ammonium Nitrate. VI. The Reciprocal Salt Pair Ammonium Nitrate and Potassium Sulphate. EDGAR PHILIP PERMAN and WILLIAM JOHN HOWELLS (T., 1923, **123**, 2128—2134).

The Diffusion of Oxygen through Silver. LEO SPENCER (T., 1923, **123**, 2124—2128).

The Crystalline Structures of Silver Iodide. R. B. WILSEY (*Phil. Mag.*, 1923, [vi], **46**, 487—496).—Employing the powder-method of *X*-ray crystal analysis, the author has determined as follows the lattice structure, length of side of the elementary structure, and distance apart of the nearest atomic centres in the cases of the respective silver halides and metallic silver:—silver chloride: simple cubic of the sodium chloride type, 5·540, 2·770 Å.; silver bromide: simple cubic of the sodium chloride type, 5·768, 2·884 Å.; silver iodide: diamond cubic of the zinc sulphide type, 6·493, 2·812 Å.; and hexagonal of the zinc oxide type, 4·593, 2·813 Å.; metallic silver: face-centred cubic, 4·078, 2·884 Å. Most of the samples of silver iodide examined showed predominance of the hexagonal structure. In some cases the cubic structure alone was evident, whilst all samples exhibited this to some extent. The axial ratio of the hexagonal structure in the case of silver was found to be 1·633±0·008. J. S. G. T.

The Preparation of Barium Alloys. V. M. GOLDSCHMIDT (*Norg. Geol. Undersökelse, Statens Raastofkomite Publication*, 1922, No. 7).—Alloys of barium with lead have been prepared by the electrolysis of fused barium chloride (8 parts), potassium chloride (5 parts), and sodium chloride (3 parts) in a cell with a carbon anode and molten lead as the cathode. The preparation of an alloy containing 10% of barium requires a temperature of 600—650°, using 4—6 volts, with electrodes 1—1·5 cm. apart, and a current density not exceeding 3 amperes/cm.^{2} at the anode and 1 ampere/cm.^{2} at the cathode. Alloys have been prepared containing 18% of barium and less than 1% of sodium; alloys with zinc and tin, of low barium content, have also been obtained.

CHEMICAL ABSTRACTS.

Reduction of some Rarer Metal Chlorides by Sodium. M. A. HUNTER and A. JONES (*Amer. Electrochem. Soc.* [advance copy], 1923, 35—41).—The anhydrous chlorides of glucinum, chromium, uranium, vanadium, and zirconium when heated with sodium in a closed steel bomb are reduced to the metal, which is generally comparatively pure and in the form of small pellets. In the case of glucinum the beads contained 99·6% of metal, *d* 1·793, m. p.

in hydrogen 1370°. The metal could not be completely burnt in air; it is readily soluble in hydrochloric acid, but is not attacked by cold concentrated nitric acid. With chromium, the product was 99·86% pure, d 6·29—6·40; it is unattacked by cold hydrochloric or sulphuric acid, but is readily attacked by either acid when heated. It is unattacked by nitric acid. In the case of uranium, powdered metal of 99% purity was obtained which oxidised slowly in the air. Similarly, vanadium was obtained as a powder of d 5·97. Zirconium gave a yield of 76% of powdered metal of 93·2% purity, d 5·29. J. F. S.

A Double Salt of Magnesium Chloride and Carbonate. TSUNEKICHI NISHIMURA (*Rikwagaku Kenkyujo Ihô*, 1923, **2**, 63—65).—The double salt, $MgCl_2,MgCO_3,6H_2O$, was prepared by passing carbon dioxide into a mixture obtained by adding calculated amounts of magnesium chloride and carbonate to 27·5% or more concentrated solution of magnesium chloride. The double salt is decomposed at once by water, but is stable towards absolute alcohol. The salt purified with absolute alcohol and dried at 40° has d^{16} 1·679. Part of the water of crystallisation is lost at 50—60°; at 100° the salt has the composition $MgCl_2,3MgCO_3,7H_2O$. A similar double salt is not formed with calcium chloride and carbonate. K. K.

Separation of Common Lead into Fractions of Different Density. R. H. ATKINSON (*Nature*, 1923, **112**, 282).—Fractional crystallisation of lead, followed by purification, yielded samples having d 11·345±0·005 and 11·313±0·005, respectively. It was observed that lead which has solidified slowly is not homogeneous as regards density, the portions which solidify first being the denser. A. A. E.

Comparison between Dilatation and Thermal Curves. L. LOSANA (*Gazzetta*, 1923, **53**, i, 393—395).—The author has applied the dilatometer described by Montemartini and Losana (this vol., ii, 373) to the study of the changes occurring during the cooling of pure tin and of tin-lead, tin-lead-cadmium-bismuth, and lead-bismuth alloys and finds that, for temperatures up to 400°, the singular points are indicated as clearly as by the ordinary cooling or heating curves. For higher temperatures, a suitable liquid with the necessary continuity in thermal dilatation is lacking. T. H. P.

Complex Formation in Lead Nitrate Solutions. I. The Ternary Systems Lead Nitrate–Sodium Nitrate–Water, and Lead Nitrate–Potassium Nitrate–Water. SAMUEL GLASSTONE and HAROLD NICHOLAS SAUNDERS (T., 1923, **123**, 2134—2140).

Rare Earth Elements in Triple Nitrites. V. CUTTICA and and F. GALLO (*Gazzetta*, 1923, **53**, i, 374—379; cf. this vol., ii, 497). —Cobalt, nickel, and copper form triple nitrites in which the other metals are an alkali metal and a metal of the cerium or yttrium group. In the cerium compounds now described, the cerous

nitrite exhibits the normal composition, $Ce(NO_2)_3$, which is not that of the isolated salt itself. Since, also, the normal nitrites of cobalt, nickel, and copper are not known, the following triple nitrites must be considered as true complex compounds.

$2Co(NO_2)_2,Ce(NO_2)_3,5KNO_2$ forms a green powder and is decomposed by water, yielding cerous nitrite and potassium cobalti-osonitrite. $2Co(NO_2)_2,Ce(NO_2)_3,5RbNO_2$, which is also green and $2Co(NO_2)_2,Ce(NO_2)_3,5TlNO_2$, which is deep brown, behave similarly towards water. These compounds, which are slowly attacked by cold, dilute acids, yielding $R_3Co(NO_2)_6$, may be represented by the general formula, $\left[Co(NO_2)_6\right]_2\begin{matrix}Ce(La,Pr,Nd,Y)\\K(Rb,Tl)_5\end{matrix}$.

As has been found in other cases, the following compounds, containing nickel or copper in place of cobalt, exhibit no general formula. $3Ce(NO_2)_3,5Ni(NO_2)_2,13KNO_2$ forms a flesh-red powder; $2Ce(NO_2)_3,6Ni(NO_2)_2,7TlNO_2$ (cf. this vol., ii, 77) has a pale chestnut colour; $3Ce(NO_2)_3,4Cu(NO_2)_2,15NH_4NO_2$ forms a black, crystalline precipitate, readily soluble in water to a green solution, remains unaltered for some time in a desiccator, but decomposes in the air with evolution of nitrous fumes; $Ce(NO_2)_3,4Cu(NO_2)_2,12KNO_2$ is similar in appearance to, but more stable in the air than, the preceding compound; $Ce(NO_2)_3,3Cu(NO_2)_2,5TlNO_2$ is the most stable of these copper complexes. T. H. P.

Some Properties of Electrolytic Manganese. ALAN NEWTON CAMPBELL (T., 1923, **123**, 2323—2327).

The Reaction between Ferrous Phosphate and Sulphur Dioxide in Phosphoric Acid Solution; the Nature of the Decomposition Products. SYDNEY RAYMOND CARTER and JOHN ALFRED VALENTINE BUTLER (T., 1923, **123**, 2380—2384).

The System Ferric Oxide–Phosphoric Acid–Water. A New Phosphate. SYDNEY RAYMOND CARTER and NORMAN HOLT HARTSHORNE (T., 1923, **123**, 2223—2233).

Electrolytic Reduction of Molybdic Acid Solutions. F. FOERSTER and E. FRICKE (*Z. angew. Chem.*, 1923, **36**, 458—460).—The electrolytic reduction of molybdic acid solutions to the quinquevalent stage and the preparations of compounds of the type $(MoOCl_5)M_2$, where M is an alkali metal or ammonia, is described. Amalgamated lead anodes were replaced by platinised platinum wire netting, as the lead was found to go into solution. The solution can also be reduced to the tervalent stage by suitable choice of acid concentration and current density. The properties of complex salts of the type $[MoCl_5,H_2O]M_2$ and $[MoCl_6]M_3$ are described. The salt $[MoBr_5,H_2O](NH_4)_2$ was also prepared. Attempts to prepare the alums and complex oxalates of molybdenum, rubidium, and cæsium were unsuccessful. Only the tervalent elements of lower atomic weight (Ti, V, Cr, Mn, Fe, Co) in this horizontal row of the periodic system appear to form easily crystallisable complex salts with bivalent anions, whereas the elements of higher atomic weight also give well crystallised complex salts with univalent

anions. The existence of the red salts, $(MoCl_6)M_3$ and $[MoCl_5,H_2O]M_2$ indicates that in the reddish-brown solutions of tervalent molybdenum an equilibrium exists between the tervalent kations and the complex ions, $(MoCl_5,H_2O)''$ and $[Mo(H_2O)_6]'''$, respectively. Considerations of static potential lead to similar conclusions. No confirmation was obtained of Chilesotti's hypothesis of an incipient reduction of tervalent to bivalent molybdenum taking place (A., 1906, ii, 263, 365). The presence of the ions $MoCl_6'''$, $(MoCl_5,H_2O)''$, and $[Mo,(H_2O)_6]'''$ is held to account for the increased reducing power of the green tervalent molybdenum solution. The fact that solutions of molybdic acid in dilute hydrochloric acid can only be reduced to the quinquevalent stage, whilst solutions in more concentrated hydrochloric acid can be reduced electrolytically to the tervalent stage, is explained by assuming that the next stage to quinquevalent molybdenum is Mo'''-ions, which in the presence of a high concentration of Cl'-ions immediately form complex ions and the static potential of the solution is reduced below that necessary for the generation of hydrogen from platinised platinum electrodes. If the concentration of chloride-ions is low, however, comparatively few complex ions are formed, and the static potential of the solution remains higher than that necessary for the evolution of hydrogen. If polished platinum electrodes are used, however, owing to the much higher potential necessary for the evolution of hydrogen, the tervalent stage can be reached even in dilute hydrochloric acid solution. The electrolytic reduction of molybdenum shows changes of potential parallel with those occurring in vanadium and titanium solutions under similar conditions. H. C. R.

Normal Thorium Molybdate, $Th(MoO_4)_2$. FERRUCCIO ZAMBONINI (*Atti R. Accad. Lincei*, 1923, [v], **32**, i, 518—524; cf. A., 1916, ii, 249).—*Thorium molybdate*, $Th(MoO_4)_2$, obtained by fusing partly dehydrated thorium chloride with excess of anhydrous sodium molybdate, forms tetragonal crystals, $a:c = 1:0{\cdot}73565$, $d^{7 \cdot 5}$ 4·92, which exhibit mutual miscibility in the solid state with cerous molybdate. The properties of the thorium salt are compared with those of other molybdates. The fact that thorium and cerium may replace one another isomorphically in such simple compounds as their normal molybdates supports the view that the element observed by Dauvillier in the mixture of rare earths containing Urbain's original celtium is identical with that encountered some months subsequently by Coster and Hevesy in certain zirconiferous minerals. T. H. P.

Bismuth Tetroxide Prepared from Sodium Bismuthate. C. E. CORFIELD and ELSIE WOODWARD (*Pharm. J.*, 1923, **111**, 80—82).—Attempts to prepare bismuthic acid and bismuth pentoxide by decomposing sodium bismuthate with nitric acid, under the most favourable conditions, were unsuccessful. If formed at all, these compounds appeared to be unstable and decomposed immediately into the tetroxide with loss of oxygen. The authors have obtained a hydrated tetroxide containing between $1H_2O$ and

$2H_2O$, but this could not be reduced to $1H_2O$ without simultaneous loss of oxygen. W. P. S.

Celtium or Hafnium? (*Chemistry and Industry*, 1923, **42**, 784—788).—A review of the facts concerned in the controversy regarding priority of nomenclature of the element of atomic number 72. On the evidence so far published, it is held that Urbain's claim to priority of discovery and to the name "celtium" should be admitted. A. A. E.

Hafnium or Celtium? BOHUSLAV BRAUNER (*Chemistry and Industry*, 1923, **42**, 884—885).—Polemical in support of Urbain's celtium. Attention is directed to the significance of the spectrographic observations of Exner and Hatschek in 1911. A. A. E.

Mineralogical Chemistry.

Chemical Relations between Humic Substances and Coal. MAURICE PIETTRE (*Compt. rend.*, 1923, **177**, 486—488; cf. *ibid.*, 139).—Extraction of Brazilian, American, or Elsecar coals with boiling pyridine, and subsequent evaporation of the solvent, gives a residue which on extraction with alcohol–ether mixtures affords an insoluble, humus-like substance (nitrogen content 2·25—2·50%), and a soluble, brown resin. The latter may be separated, by extraction with alkalis, into acidic and tarry substances.

Cardiff coal gives no appreciable pyridine extract, and is therefore to be regared as a completely mature coal. On treatment with nitric acid (*d* 1·40), it affords a highly combustible nitrated product, which, after reduction in presence of alkali, gives a black substance (nitrogen content about 4·45%) possessing most of the properties of humus. This suggests a common origin for humus, peat, and coal. E. E. T.

Japanese Minerals containing Rarer Elements. V. Analysis of Beryl from Ishikawa, Ishikawa Province. TAKU UYEMURA (*J. Chem. Soc. Japan*, 1923, **44**, 296—302).—The analysis of beryl produced in Ishikawa, Ishikawa Province, opaque, slightly green crystals, *d* 2·8, gave the following results:

SiO_2.	GlO.	Fe_2O_3.	Al_2O_3.	CaO.	MgO.	Alkali (as Na_2O).	Loss by heating.	Total.
49·60	19·31	0·11	24·09	0·79	0·14	3·65	2·81	100·50

By spectrum analysis silicon, glucinum, iron, aluminium, calcium, magnesium, scandium, and sodium, but not chromium were detected. The formula $4GlO,Al_2O_3,4SiO_2$ and a constitutional formula are proposed; in the latter, one molecule of silicic acid is expressed as ortho-acid. In the present case, Copaux's method (A., 1919, ii, 192) was useless for the estimation of glucinum. K. K.

Clays. I. The Acidic Reaction of Japanese Acid Clays. TSURUJI OKAZAWA (*Rikwagaku Kenkyujo Ihô*, 1923, **2**, 189—221).—When treated with a neutral salt solution, Japanese acid clay gives an acidic reaction to the solution, a phenomenon which K. Kobayashi ("Japanese Acid Clay," Tokyo, 1922; *J. Chem. Ind. Japan*, 1923, **26**, 289) has attributed to its large adsorptive action, but the author has put forward a different explanation. Clays may be classified into three kinds according to their reactivity with salt solutions and acids. The first group gives no dissolved part by treatment with salt solutions and only a slight amount with strong acids; the second yields none by the salt solution, but a large quantity by the acid; and the third, which includes Japanese acid clay, gives a large amount by both the solutions. When treated with salt solutions, clay particles absorb positive radicles, aluminium being dissolved as the corresponding salt, *e.g.*, $R{:}Al{\cdot}OH + MgCl_2 = RMg + AlCl_2{\cdot}OH$, and $AlCl_2{\cdot}OH + 2H_2O = Al(OH)_3 + 2HCl$. This reaction is therefore attributed partly to adsorption, but mainly to double decomposition, and the acidity is governed by the salt used, adsorptive and reactive affinities of the clay, stability of the reaction product, reaction velocity, etc.

The acidity is therefore not definitely determined by titrating with alkali solution, and reaction will be as follows (when a chloride is used as a salt): $AlCl_2{\cdot}OH + 2H_2O = Al(OH)_3 + 2HCl$; or $AlCl_3 + 3H_2O \rightleftarrows 3HCl + Al(OH)_3$; $AlCl_2{\cdot}OH + 2NaOH = Al(OH)_3 + 2NaCl$; or $AlCl_3 + 3NaOH \rightarrow Al(OH)_3 + 3NaCl$. Aluminium hydroxide thus produced will further react with alkali.

When the clay is burned, the so-called acidity is decreased and almost completely removed in one hour at 700—800°. By the action of heat the state of molecular aggregation will be changed and the aluminium oxide in the clay will not be dissolved by salt solutions. But a reverse relation exists between the temperature of burning and the quantity of aluminium oxide dissolved by acids; the quantity dissolved attains a maximum value at about 700—800°, and decreases rapidly above 900°. K. K.

Oxydase Reaction of Japanese Acid Clay, Fuller's Earth, and Florida Earth. KYUHEI KOBAYASHI and KEN-ICHI YAMAMOTO (*J. Chem. Ind. Japan*, 1923, **26**, 289—296).—Japanese acid clays, fuller's earth, and Florida earth, but not kaolin, kieselguhr, or volcanic ash, give the oxydase reaction with an alcoholic solution of guaiacum, and with other substances. It is supposed that the so-called Helmholtz double layer is formed around the surface of the clay when suspended in water and that it absorbs hydroxyl-ions, hydrogen-ions being liberated near the surface. The hydroxyl-ions thus absorbed combine directly, liberating one atom of oxygen and forming water. This active atom of oxygen may act on oxidisable reagents and give the oxydase reaction. K. K.

Analytical Chemistry.

A New Colorimeter having Perfectly Symmetrical Light Distribution. K. Bürker (*Z. angew. Chem.*, 1923, **36**, 427—429).—Two parallel beams of light pass upwards through equal and variable thicknesses of, respectively, pure solvent and the coloured solution under examination, and then through 10 mm. of standard colour solution and pure solvent, respectively. They are brought together by means of an Albrecht-Hüfner hexagonal lens and appear in the eyepiece of the instrument as two semicircular fields separated by a narrow boundary line. [Cf. *J.S.C.I.*, 1923, Oct.]
W. T. K. B.

[Use of] the Gooch Crucible. Archibald Craig (*Chem. Age* [*N.Y.*], 1923, **31**, 31—32).—The importance of rapidly filtering asbestos is emphasised. A modified form of bell-jar for filtering directly into a beaker is described. To enable a pencil to be used for marking crucibles, the surface of the porcelain is roughened by application of a paste of barium sulphate and hydrofluoric acid. For calculating results of gravimetric analyses, an empirical factor, dependent on the conditions of the estimation, should be used instead of the theoretical factor. Chemical Abstracts.

A New Explosion Pipette. K. Tiddy (*Gas World*, 1923, 79, 187).—A modification of the Hempel explosion pipette employed in gas analysis, which eliminates leakage of gas under the pressure developed by the explosion, and is more robust than the customary form, is described. In this, the U-shaped exit tube connected by a rubber joint with the capillary of the measuring vessel is replaced by a straight capillary tube and stop-cock. The device can be readily incorporated in a gas analysis apparatus of the Orsat type.
J. S. G. T.

Carbinols as Indicators. L. Karczag and R. Bodó (*Biochem. Z.*, 1923, **139**, 342—344).—The colourless carbinols of certain triphenylmethane dyes (*e.g.*, red-violet, fuchsin-S, water-blue) may be utilised as indicators, since on the addition of acid they are immediately converted into the coloured ammonium bases. The carbinols were obtained by decolorising solutions of the dyestuffs with stick charcoal, and by using these with buffer solutions according to Sörensen's method it was found that water-blue has a range from p_H 5·0 to 6·2, the colour development being instantaneous at the higher hydrogen-ion concentration and requiring from ten to fifteen minutes at the lower value. Fuchsin-S showed a similar but more rapid change over a range from p_H 5·2 to 6·6. J. P.

The Colorimetric Estimation of Hydrogen-ion Concentration by the Method of Michaelis, with One Colour Indicators, using Inorganic Comparison Solutions. I. M. Kolthoff (*Pharm. Weekblad*, 1923, **60**, 949—966).—In view of the

application of the method of Michaelis and his co-workers (A., 1921, ii, 56; *Biochem. Z.*, 1921, **109**, 307) to the examination of urine, drinking-water, and other biologically important liquids, a critical examination has been made of his results. The low buffer capacity of his solutions renders the accuracy of his figures questionable, and the necessity of preparing for each series of determinations a great number of comparison solutions of the indicators makes his method cumbrous. The constants of the indicators have now been redetermined, using the buffer mixture solutions of Clark, which have also been checked potentiometrically.

The indicators 2 : 4-, 2 : 5-, and 2 : 6-dinitrophenol, *m*- and *p*-nitrophenol, and salicyl-yellow have thus been examined, and the constants with their temperature coefficients now determined show good agreement with those given by Michaelis, except in the case of *p*-nitrophenol, for which $p_H = 7{\cdot}04$, a value considerably below the figures given in the literature.

In place of the alkaline solutions of the indicators themselves, solutions of potassium chromate (for 2 : 4-dinitrophenol and *p*-nitrophenol) and dichromate (2 : 5-dinitrophenol, *m*-nitrophenol, and salicyl yellow) and mixtures of the two (2 : 6-dinitrophenol) may be more conveniently employed as comparison solutions, and details are given of the concentrations and quantities corresponding with the colour of definite indicator solutions. S. I. L.

Estimation of Total Sulphur in Biological Material. MABEL STOCKHOLM and FRED C. KOCH (*J. Amer. Chem. Soc.*, 1923, **45**, 1953—1959).—The dry fusion method for the estimation of sulphur in organic material tends to give low and irregular results when properly corrected for blanks; this is due to loss of reduced sulphur by volatilisation during the heating of the dry mixture, the loss being greater the more rapidly the temperature is increased (cf. Barlow, A., 1904, ii, 82). It is found that the following procedure gives the calculated value for cystine, and uniform results, usually higher than by the fusion method, with different biological materials containing organically combined sulphur. 0·5—2 G. of material and 10 c.c. of 25% sodium hydroxide solution are slowly evaporated on the steam-bath until almost dry; 5 c.c. of 30% hydrogen peroxide solution are then very gradually added, the heating being meanwhile continued. The partly oxidised material is now acidified by means of nitric acid, and concentrated more rapidly until crystallisation commences. The boiling solution is oxidised by the gradual addition of 10 c.c. of fuming nitric acid and 40—50 drops of bromine. In the analysis of lipin materials, *e.g.*, nerve-tissue or egg-yolk, the treatment with nitric acid and bromine is prolonged during twenty-four hours. The solution is evaporated almost to dryness, water is added, and the evaporation repeated, to remove most of the nitric acid. The aqueous solution, filtered if necessary, is neutralised by means of sodium hydroxide, diluted to about 600 c.c., and acidified by means of 10 c.c. of concentrated hydrochloric acid. The sulphate is estimated in the usual way, after the addition of 10 c.c. of $0{\cdot}1N$-sulphuric acid. This addition of a

standard quantity of sulphuric acid in estimations of sulphate, including blanks, is recommended, because in this way the complete precipitation of small traces of sulphate is promoted. W. S. N.

Detection of Nitrites by Rodillon's Test. HANS HELLER (*Chem. Ztg.*, 1923, **47**, 701).—Leffmann's failure to obtain consistent results in Rodillon's test for nitrites in water (this vol., ii, 37) was due to his use of hot sulphuric acid for dissolving the resorcinol (*Amer. J. Pharm.*, 1923, **95**, 110). If the cold acid is used and the reagent freshly prepared for each test trustworthy results are always obtained; on keeping, the solution slowly deposits crystals and is then useless. The following modification of the original method is recommended: 0·4 g. of resorcinol is shaken with 5 c.c. of cold, concentrated sulphuric acid and 1 c.c. of this solution is carefully poured below the surface of 5 c.c. of the water to be tested. At the interface between the liquids a green, violet, or blue colour appears, according to the concentration of the nitrite. The reagent crystallises after eight hours; for further use, a few drops of water are added and the whole is warmed until the crystals dissolve, and then cooled. A. R. P.

Estimation of Phosphorus in Light Aluminium Alloys. L. LOSANA and C. E. ROSSI (*Annali Chim. Appl.*, 1923, **13**, 200—204). —The estimation of sulphur or phosphorus in aluminium alloys containing 1% of either copper or tin should be effected by the oxidation method and not by treating the metal with hydrochloric acid and estimating the hydrogen sulphide or phosphide liberated; zinc, however, does not interfere with the latter method. T. H. P.

The Micro-estimation of Phosphoric Acid. RICHARD KUHN (*Z. physiol. Chem.*, 1923, **129**, 64—79).—The micro-estimation of phosphoric acid is best carried out gravimetrically by weighing the precipitate obtained on precipitation with ammonium molybdate. The alkalimetric titration is not satisfactory except with very small quantities of material. Separation of arsenic from phosphorus is best carried out by distillation of the arsenic in a stream of hydrogen chloride. The phosphorus is then estimated either gravimetrically or, if there is less than 0·04 mg., nephelometrically (cf. Kleinmann, *Biochem. Z.*, 1919, **99**, 115, 150). W. O. K.

Chemistry of the Reinsch Test for Arsenic and Antimony and its Extension to Bismuth. B. S. EVANS (*Analyst*, 1923, **48**, 357—367).—The tests were carried out by comparing the colour of the film deposited on a cleaned and polished surface of electrolytic copper suspended in the solution to be tested by means of a glass stirrup, with a standard copper-arsenic or copper–antimony alloy similarly suspended in the same beaker, but enclosed in a smaller interior beaker containing distilled water. The time taken for the electrolytic copper surface to assume the same appearance as the standard alloy under different conditions as regards concentrations of sodium chloride, sulphuric acid, arsenic, antimony, or bismuth, and cupric-ions was noted. For arsenic tests, a 70 : 50 copper–arsenic alloy polished and etched with nitric

acid (d 1·2) was used, and a 50 : 50 copper–antimony alloy, similarly treated, was used for the antimony tests. For the bismuth tests, a 90 : 10 copper–arsenic alloy, polished but not etched, was employed. The results of varying the factors mentioned above one at a time are given in a series of tables. Increase of sodium chloride concentration increases the rate of formation of the standard film markedly in the case of arsenic and antimony, less so in the case of bismuth. Increase of sulphuric acid concentration also increases the rate of formation of the film, but in all three tests there is a certain concentration of acid above which further additions are without influence on the rate of reaction. These concentrations are for arsenic, antimony, and bismuth, respectively, 5·47%, 2·74%, and 2·28%. The presence of cupric-ions in the solution retards the formation of the film to such an extent that any considerable concentration may be said to inhibit it, but cuprous-ions which are formed during the reaction itself have no such action. The film formed in the test for arsenic was analysed, and consisted chiefly of the compound Cu_5As_2, with the addition of a little elementary arsenic deposited electrolytically. In the case of the bismuth reaction, only a trace of copper was found in the film. The separation of the antimony film presented great difficulty. The initial purple film probably consists of the compound Cu_2Sb, but the composition of the subsequently formed white film could not be determined. H. C. R.

Estimation of Boric Acid by the Hönig-Spitz Method. HANS RATH (*Naturprodukte*, 1923, 134—139).—A detailed account of the method of titrating boric acid with sodium hydroxide in presence of glycerol. E. H. R.

Estimation of the Content of Active Carbon Dioxide in Drinking Waters. P. LEHMANN and A. REUSS (*Z. Unters. Nahr. Genussm.*, 1923, **45**, 227—236).—A consideration of the work of Schlœsing (*Compt. rend.*, 1872, **74**, 1552; **75**, 70) and the application of the law of mass action leads to the deduction of the following formula for calculating the combined carbon dioxide (c) in a sample of drinking water from the total carbon dioxide (t) determined in mg. per litre: $c=27[\sqrt[3]{t+\sqrt{t^2+5823}}+\sqrt[3]{t-\sqrt{t^2+5823}}]$. If, however, t exceeds 200, a correction is necessary on account of the carbonate not being completely dissociated at higher concentrations. This correction factor is deduced to be $2772 \cdot 9/(2886-c)$. A table is given of the sums of combined and active carbon dioxide concentrations corresponding with experimentally determined total carbon dioxide concentrations, calculated by means of the above formula, the correction factor being applied where necessary. Details are given of methods of estimating the combined and free carbon dioxide by titrations with hydrochloric acid, using methyl-orange as indicator, and with sodium carbonate, using phenolphthalein as indicator, respectively. The active carbon dioxide in water containing calcium sulphate must be estimated directly by experiments on powdered

marble according to von Heyer's method (*Gesundheitsingenieur*, 1912, **35**, 675; see also Kolthoff, A., 1921, ii, 59). H. C. R.

The Estimation of Alkalis in Rocks by the Indirect Method. Frederick Walker (T., 1923, **123**, 2336—2341).

Estimation of Potassium by the Perchlorate and Cobaltinitrite Methods, and the Removal of Sulphates. R. Leitch Morris (*Analyst*, 1923, **48**, 250—260; cf. A., 1920, ii, 707).—The perchlorate method is trustworthy for the estimation of potassium in the presence of phosphates, but sulphates and ammonium salts must be removed previously. It is recommended that the sulphate should be precipitated as barium sulphate from a strongly hydrochloric acid solution and that the barium sulphate precipitate should be ignited and extracted with hot hydrochloric acid, the acid extract being added to the main solution. The potassium perchlorate precipitate should be washed first with alcohol containing 0·2% of perchloric acid and then with this alcohol-perchloric acid mixture saturated previously with potassium perchlorate. Drushel's modification of the cobaltinitrite method (A., 1908, ii, 66) also yields trustworthy results provided that, in the oxidation of the precipitate, a considerable excess of permanganate solution is used and the mixture heated for ten minutes before the sulphuric acid is added; the heating should be continued for a further ten minutes before the oxalic acid is added.

W. P. S.

New Method of Analysing Sodium Hyposulphite. S. H. Wilkes (*J. Soc. Chem. Ind.*, 1923, **42**, 356—357T).—Sodium hyposulphite is estimated by determination of the amount of iodine liberated from excess of an iodate–iodide mixture according to the equation $3Na_2S_2O_4+4KIO_3+2KI=3I_2+3Na_2SO_4+3K_2SO_4$. The iodine liberated is not titrated directly with thiosulphate, but excess of the latter is used and the quantity unused is determined by back titration with standard iodine. The method is not applicable to samples of hyposulphite containing soda-ash or decomposition products. H. H.

Estimation of Calcium in Plasma. A. Hirth (*Compt. rend. Soc. Biol.*, 1923, **88**, 458—460; from *Chem. Zentr.*, 1923, ii, 1099).—The ash from 5 c.c. of plasma is dissolved in 2 c.c. of 7% hydrochloric acid. Four drops of 4% ferric chloride solution and one drop of bromine water are added, and the liquid is heated to boiling. After cooling and diluting to 15 c.c., ammonia is added until the liquid is alkaline to phenolphthalein. A slight excess of acetic acid is added and the ferric phosphate and basic ferric acetate are removed by filtration; the precipitate is washed with water containing ammonium acetate and acetic acid. The neutralised filtrate is concentrated to about 4 c.c. and the calcium precipitated as calcium oxalate. G. W. R.

Estimation of Magnesium in Plasma. A. Hirth (*Compt. rend. Soc. Biol.*, 1923, **88**, 460—461; from *Chem. Zentr.*, 1923, ii, 1099).—The filtrate from the estimation of calcium (see pre-

ceding abstract) is evaporated to dryness and heated to remove ammonium compounds. The residue is dissolved in hydrochloric acid. After addition of ammonia solution, the magnesium is precipitated by addition of ammonium phosphate solution. The precipitate after washing is dissolved in nitric acid containing sulphuric acid. Ammonium molybdate is added to precipitate the phosphate (Lorenz-Pregl). The precipitate of ammonium phosphomolybdate is then dissolved in ammonia solution and precipitated with 2 c.c. of 10% barium chloride solution (Posternak). This precipitate after collection is incinerated and weighed. The factor used for conversion to magnesium is 0·00579. G. W. R.

A New Reaction for Zinc. G. SPACU (*Bul. Soc. Ştiinţe Cluj*, 1922, **1**, 348—351; from *Chem. Zentr.*, 1923, ii, 1052).—The reaction proposed depends on the insolubility of the compound $[Zn(C_5H_5N)_2](CNS)_2$. It takes place preferably in neutral solution or with a slight excess of pyridine. With great excess of pyridine the precipitate redissolves. One part of zinc in 200,000 parts of water may be detected. G. W. R.

Estimation of Cobalt in Special Steels. GIULIO FERRERI (*Giorn. Chim. Ind. Appl.*, 1923, **5**, 339—340).—The tungsten and silicon are removed from the solution as oxides and the cobalt separated as potassium cobaltinitrite and estimated electrolytically. [Cf. *J.S.C.I.*, 1923, Oct.] T. H. P.

Estimation of Chromium in Presence of Organic Matter. G. GRASSER (*Z. Leder-u. Gerb.-Chem.*, 1922—1923, **2**, 185—188).—The treatment of chromium residues with sulphuric acid and potassium permanganate to destroy organic matter prior to the iodometric estimation of the chromium gives concordant results, but not with iron alum solution. The Fresenius-Babo method of oxidising with sulphuric acid and potassium chlorate gives good results with iron alum and iodometrically. Potassium chlorate and hydrochloric acid, also chloric acid, have been used to oxidise the organic matter, in some cases completing the oxidation with ammonium persulphate. The quickest and best method of oxidation consists in heating a mixture of 10 parts of the chromium residue, 3 parts of potassium nitrate, and 1 part of calcined sodium carbonate to dryness and then fusing to oxidise the chromium to chromate. The fused mass is extracted with hot water, acidified, and the chromium estimated iodometrically or with iron alum. D. W.

Uses of Amalgams in Volumetric Analysis. VIII. Estimation of Chromium and of Iron in the Presence of Chromium. NAOTSUNA KANO (*J. Chem. Soc. Japan*, 1923, **44**, 37—46).—Chromium was estimated volumetrically after reduction with ferrous or titanous sulphate, which was prepared by reducing with zinc amalgam. A definite quantity of titanic sulphate was reduced to the titanous salt with zinc amalgam, potassium chromate was added until the colour of chromium-ion appeared, and the remaining ter-

valent titanium was titrated with about 0·1*N*-iron alum solution, using ammonium thiocyanate as indicator. Towards the end, the solution should be warmed at 50°. 0·1*N*-Potassium permanganate may be used instead of iron alum solution. A definite quantity of iron alum may be used instead of titanic sulphate and the remaining bivalent iron titrated with 0·1*N*-potassium permanganate solution. When the quantity of chromium is large, *e.g.*, 0·03 g. of the oxide in 100 c.c., the first method is the most accurate. When less chromium is present, a definite quantity of titanic sulphate can be reduced to titanous salt, a mixture of potassium chromate and iron alum in different proportions added, and the chromium titrated with potassium permanganate. Chromium may also be estimated by the same method, using iron alum instead of titanic sulphate. Iron in presence of chromium is estimated as follows. A mixture of iron and chromium salts is reduced with zinc amalgam in the presence of carbon dioxide. When reduction is complete, the carbon dioxide is replaced by air and the liquid shaken for a few minutes; chromium is completely changed into the tervalent form, and the bivalent iron is titrated with 0·1*N*-potassium permanganate solution; the quantity of chromium should be limited to 0·03 g. of the oxide in 100 c.c. of solution. K. K.

Uses of Amalgams in Volumetric Analyses. IX. Estimation of Titanium and of Iron in the Presence of Titanium. NAOTSUNA KANO (*J. Chem. Soc. Japan*, 1923, **44**, 47—53; cf. *ibid.*, 1922, **43**, 544, 547, 554, 555).—Titanium and iron are estimated volumetrically without separation. A mixture of iron alum and titanium sulphate is reduced with zinc amalgam and titrated with 0·1*N*-potassium permanganate, by which the sum (s) of the titanium and iron is determined. Next a definite volume (a c.c.) of the mixture of iron alum and titanium sulphate is reduced with zinc amalgam and titrated with the unreduced mixture (b c.c.) using ammonium thiocyanate as indicator; tervalent iron in the latter mixture oxidises tervalent titanium in the reduced mixture. Then the ratio of the concentrations $c_{Fe}/c_{Ti}=a/b$, and $c_{Ti}(1+a/b)=s$. K. K.

Estimation of Antimony and its Separation from Tin. P. WENGER and G. PARAUD (*Ann. Chim. Analyt.*, 1923, [ii], 5, 230—232).—The methods of Henz (A., 1904, ii, 150), Wortmann and Metzel (A., 1905, ii, 655), Bunsen and Baubigny (A., 1897, ii, 351), and Classen for the estimation of antimony gave results varying between 99·34% and 99·79% of the theoretical. Rose's method, however, gave very low results and is not considered to be of any value for exact estimations. Wortmann and Metzel's and Classen's methods are the most convenient and rapid. In separating antimony from tin, Clarke's method (*Chem. News*, **21**, 124) and Tomula's method (A., 1922, ii, 74) were found satisfactory, but Rose's method is again useless. H. C. R.

Detection of Methyl Alcohol in Ethyl Alcohol. R. MEURICE (*Ann. Chim. Analyt.*, 1923, [ii], **5**, 204—205).—Ten c.c. of the

95% alcohol are mixed at 18° with 10 c.c. of 22% ammonium sulphate solution; in the case of pure ethyl alcohol, the mixture separates into two clear layers within about two minutes, but if the alcohol under examination contains 3% of methyl alcohol the lower layer is turbid and contains crystals of ammonium sulphate. In the presence of 10% of methyl alcohol, a voluminous precipitate of ammonium sulphate is formed. W. P. S.

The Detection of Methyl Alcohol in Alcoholic Liquids. VAN RIJN (*Pharm. Weekblad,* 1923, **60**, 978—984).—Samples of spirits suspected to contain methyl alcohol were examined by (1) Mannich and Fendler's method, (2) method of Pfijl, Reif, and Hanner, and (3) Riche-Bardy's method, the results being checked by determination of the refractive indices of the absolute alcohol obtained by distillation over calcium oxide. All these methods gave parallel results, but owing to the time required for (3), the first two are more suitable.

From 500 c.c. of the original sample half was distilled, from the distillate half again, and so on until 15 c.c. only of distillate was left, each fraction and the original sample being tested by the three methods. In all cases positive results were obtained from the original sample, and sometimes from the first distillate, but never from the fourth and fifth distillates. Since methyl alcohol concentrates in the final fractions, as was confirmed by adding 0·5% to one sample, it is evident that positive results are given by substances other than this alcohol (higher alcohols or ethers ?), in testing for which, accordingly, it is necessary to fractionate repeatedly. The refractive index of the anhydrous alcohol affords a valuable check. S. I. L.

Critical Examination of Methods for the Estimation of Lævulose in the Presence of Dextrose. H. COLIN (*Bull. Assoc. Chim. Sucr.*, 1923, **40**, 397—405).—The methods investigated were (1) the polarimetric method; (2) oxidation of the dextrose by bromine, (3) oxidation of the dextrose by iodine; (4) conversion of the dextrose into methyl glucoside; (5) destruction of the lævulose by heating at 100° for three hours with 7% hydrochloric acid; and (6) detection of lævulose by precipitating it as its calcium compound. All these methods yielded trustworthy results when applied to the pure sugars alone, but not in the case of complex mixtures such as plant extracts. The latter contain substances which interfere particularly with the polarimetric, bromine, and iodine methods. W. P. S.

Estimation of Starch. FRANZ TEMPUS (*Naturprodukte*, 1923, 52—58).—The difficulties attending the accurate estimation of starch in vegetable materials can be overcome by means of a preliminary heating with strong ammonia solution. This treatment brings about disruption of the cell-walls, frees the starch granules, and facilitates the removal of sugars, dextrin, hemicelluloses, and fats. A dried sample, not more than 2 g., is finely powdered and warmed for three hours in a stoppered glass vessel

at 40—45° with 50 c.c. of concentrated ammonia. It is then filtered through a linen filter on a Gooch crucible and washed well. The residue is then finely ground and the starch estimated by the diastase method. E. H. R.

Estimation of Starch. II. Estimation of Starch in Potatoes. ARTHUR R. LING and W. J. PRICE (*J. Inst. Brewing*, 1923, 29, 732—734; cf. A., 1922, ii, 879).—A curve, similar to that given for barley and wheat starches, has now been obtained showing the dependence of the proportion of apparent maltose yielded by potato starch on the diastatic power of the malt used to effect the starch conversion. The two curves are almost parallel, the percentages of maltose being higher for potato starch than for barley and wheat starches.

To estimate the starch in potatoes, about 8 g. of the finely sliced tubers are weighed exactly and pounded in a glass mortar, the pulp being washed into a beaker with about 100 c.c. of water and left for thirty minutes with occasional stirring. The supernatant liquid is then decanted on to a No. 41 Whatman filter and another 100 c.c. of water are added to the pulp and decanted at the end of thirty minutes, the pulp and filter being well washed with water. The filter and its contents are boiled in the beaker containing the pulp with 100 c.c. of water for ten minutes, and the gelatinised starch is afterwards hydrolysed at 57° by treatment for an hour with 10 c.c. of the extract of a malt of known diastatic power. The liquid is then boiled, cooled, and made up to 200 c.c., an aliquot portion being then titrated with Fehling's solution. T. H. P.

Estimation of the Eugenol Content of Volatile Oils by Titration. P. N. VAN ECK (*Pharm. Weekblad*, 1923, 60, 937—940).—A weighed quantity of clove or other eugenol-containing oil is heated with excess of standard ammoniacal silver nitrate solution, the excess of silver nitrate being estimated after filtration by titration with standard thiocyanate solution. One part of eugenol is found by experiment to cause the separation of 1·75 parts of silver. S. I. L.

Estimation of Simple, Soluble Cyanogen Compounds, Making Use of the Principle of Aëration. JOSEPH H. ROE (*J. Amer. Chem. Soc.*, 1923, 45, 1878—1883).—An aëration process for estimating cyanides has been devised, in which the liberated hydrocyanic acid is swept by a current of air into a dilute solution of an alkali hydroxide and the mixture then titrated with standard silver nitrate solution, using a little potassium iodide solution as indicator. In the case of a soluble cyanide, the procedure is as follows: a quantity of the cyanide (0·05 g.) is dissolved in 100 c.c. of water and placed in a cylinder of 200 c.c. capacity fitted with a doubly bored stopper. Through one hole, a glass tube, which reaches to the bottom of the cylinder, is placed and a glass exit tube passes through the other hole. The exit tube is connected with a double bubbler apparatus containing about 100—150 c.c.

of 5% sodium hydroxide. A few drops of amyl alcohol are added to the cyanide solution to prevent foaming. The apparatus is connected to a water pump and a slow current of air drawn through, and at the same time 25 c.c. of saturated tartaric acid solution are added to the cyanide. Air is drawn through at the rate of 3 litres per minute for two to three hours. The alkaline solution is then treated with 10 drops of 10% potassium iodide and titrated with $0{\cdot}01N$-silver nitrate solution until a faint turbidity is produced. The method has been applied to the case of mercuric cyanide. In this case, a few crystals of sodium chloride are added to the solution of mercuric cyanide and then, in addition to the tartaric acid which is added as before, 10 c.c. of 5% stannous chloride are added and the process is carried out as described. The present method has many advantages over the older distillation methods, among which may be noted the absence of loss due to hydrolysis of the hydrocyanic acid and its power of estimating cyanides in the presence of ferrocyanides and ferricyanides. The results are highly accurate. J. F. S.

Potassium Ferrocyanide as a Reagent in the Microscopic Qualitative Chemical Analysis of the Common Alkaloids. HOWARD IRVING COLE (*Philippine J. Sci.*, 1923, **23**, 97—101).—Potassium ferrocyanide forms definite crystalline compounds with certain alkaloids (cf. Cumming, T., 1922, **121**, 1287) and may be used for their microchemical detection. A small drop (2 to 3 mm. diameter) of the solution of the alkaloid in hydrochloric acid is placed on the microscope slide near a smaller drop of a 5% solution of potassium ferrocyanide and a narrow channel between the drops is made by means of a platinum wire; after a short time the preparation is vigorously scratched with the wire to induce crystallisation. β-Eucaine yields, under these conditions, thin elongated hexagonal or rhombic plates which exhibit parallel and symmetrical extinction under crossed nicols; brucine gives highly refractive prisms arranged in rosettes and exhibiting strong polarisation; cinchonidine gives rosettes of yellow, curving, hair-like needles, cinchonine, yellow, irregular, trapesium-shaped crystals which polarise strongly, and cocaine, irregular, six-sided plates and prisms which grow much thicker, polarise more strongly, and are more irregular in shape than those of the β-eucaine compound. The coniine compound crystallises in rosettes of colourless needles, which polarise weakly, exhibiting oblique extinction, that of heroin in spheroidal crusts only from concentrated solutions and that of hydrastine in spheroidal crusts which are polarised under crossed nicols. The crystals obtained from quinoline are lemon-yellow rhombohedra exhibiting parallel and oblique extinction, those from sparteine are colourless rhombs giving symmetrical extinction, and those of stovaine are rosettes of needles showing parallel extinction. Potassium ferrocyanide in hydrochloric acid solution affords a very sensitive test for strychnine, with which it gives long, slender needles or spear-shaped crystals with serrated edges and exhibiting oblique extinction. Veratrine yields an amorphous

precipitate under these conditions and, although this crystallises slowly, the test is unsatisfactory in this case. A. R. P.

Evaluation of the Catalytic Power of Diastases. L. MATHIEU (*Bull. Assoc. Chim. Sucr.*, 1923, **40**, 423—426).—The method proposed consists in mixing 10 c.c. of the diastase solution (vegetable or other extract) with 5 c.c. of hydrogen peroxide in a suitable apparatus and measuring the volume of oxygen liberated within one minute. It is suggested that the catalytic value be expressed as the ratio between the volume of oxygen thus found and that obtained when 1 g. of manganese dioxide is treated under the same conditions. The manganese dioxide used should pass a 100-mesh sieve; the hydrogen peroxide (12 vol.) should be treated previously with sodium hydroxide so that 90% of its acidity is neutralised. W. P. S.

Pancreatic Enzymes. IV. The Stalagmometric Estimation of Hydrolysis of Tributyrin by Lipase. RICHARD WILLSTÄTTER and FRIEDRICH MEMMEN (*Z. physiol. Chem.*, 1923, **129**, 1—25).—The estimation of lipase may be carried out conveniently by measuring with a stalagmometer the change in a given time in the "drop-number" of a saturated aqueous solution of tributyrin. It is found that albumin inhibits the hydrolysis of tributyrin by lipase in acid and in alkaline media, whilst albumin inhibits the hydrolysis of olein in an acid and accelerates it in an alkaline medium. This is because the sodium oleate produced increases the rate of hydrolysis by lipase. The rate of hydrolysis of tributyrin is increased by the presence of sodium oleate or sodium glycocholate, but more particularly by calcium oleate. It is suggested that the inhibition due to albumin is caused by the adsorption of one component only (the lipase), whilst in the presence of soaps, both components are adsorbed. The measurements of the amount of lipase present, obtained by the tributyrin method, are not always identical with those obtained from the hydrolysis of olein, although they are approximately so for lipase from pig's or sheep's pancreas. A tributyrin unit is therefore suggested—the amount which will cause a decrease of 20 drops, *i.e.*, about half the difference between the drop number of pure tributyrin solution and of pure water, in fifty minutes under specified conditions. For such estimations, the lipase is activated by sodium oleate, calcium chloride, and albumin, and brought to p_H 8·6, and a temperature of 20°.

The polypeptide, leucylglycylglycine, very markedly increases the rate of hydrolysis of tributyrin by lipase. If albumin, calcium chloride, and sodium oleate, however, are there previously, the tripeptide has little effect. The hydrolysis of olein or methyl butyrate in presence of calcium oleate is markedly increased by albumin, but that of tributyrin under similar conditions is not. W. O. K.

General and Physical Chemistry.

Some Refractive Indices of Benzene and *cyclo*Hexane. J. W. Gifford and T. M. Lowry (*Proc. Roy. Soc.*, 1923, [*A*], **104**, 430—437).—Values of the refractive indices of benzene and *cyclo*hexane at 15°, for about twenty wave-lengths between 7701·92 and 2980·75 Å., have been determined to the seventh significant figure, by the method of the hollow prism. In the case of *cyclo*hexane, the refractive index, n, corresponding with the wave-length λ, is, in the case of wave-lengths other than 3261·17 and 3252·65 Å., given with an average error equal to 0·00006, by the equation

$$n^2=2\cdot011046+0\cdot0102467/(\lambda^2-0\cdot013977).$$

In the case of the two wave-lengths referred to, the respective differences between experimental and calculated values of n are +0·00121 and +0·00130. No corresponding relation holds in the case of benzene, a result which is in accord with the more complex chemical structure of this substance. J. S. G. T.

Spectrochemistry of Tropane Derivatives. K. von Auwers (*J. pr. Chem.*, 1922, [ii], **105**, 102—119).—The following data are recorded. Tropane has $d_4^{10\cdot5}$ 0·9386, $n_\alpha^{10\cdot5}$ 1·47950, $n_D^{10\cdot5}$ 1·48187, $n_\beta^{10\cdot5}$ 1·48845, $n_\gamma^{10\cdot5}$ 1·49394, $d_4^{21\cdot6}$ 0·9307, $n_\alpha^{21\cdot6}$ 1·47427, $n_D^{21\cdot6}$ 1·47659, $n_\beta^{21\cdot6}$ 1·48318, $n_\gamma^{21\cdot6}$ 1·48854. Tropidine has $d_4^{18\cdot4}$ 0·9535, $n_\alpha^{18\cdot4}$ 1·48752, $n_D^{18\cdot4}$ 1·49037, $n_\beta^{18\cdot4}$ 1·49793, $n_\gamma^{18\cdot4}$ 1·50417, $d_4^{10\cdot5}$ 0·9609, $n_\alpha^{10\cdot5}$ 1·49199, $n_D^{10\cdot5}$ 1·49486, $n_\beta^{10\cdot5}$ 1·50257, $n_\gamma^{10\cdot5}$ 1·50898. Tropine has $d_4^{99\cdot8}$ 1·0161, $n_\alpha^{99\cdot8}$ 1·47917, $n_D^{99\cdot8}$ 1·48113, $n_\beta^{99\cdot8}$ 1·48766, $n_\gamma^{99\cdot8}$ 1·49269. Acetyltropein has $d_4^{15\cdot4}$ 1·0627, $n_\alpha^{15\cdot4}$ 1·47456, $n_D^{15\cdot4}$ 1·47687, $n_\beta^{15\cdot4}$ 148321. Propionyltropein has $d_4^{19\cdot6}$ 1·0399, $n_\alpha^{19\cdot6}$ 1·47208, $n_D^{19\cdot6}$ 1·47434, $n_\beta^{19\cdot6}$ 1·48069, $n_\gamma^{19\cdot6}$ 1·48591. Tropinone has $d_4^{99\cdot6}$ 0·9872, $n_\alpha^{99\cdot6}$ 1·45975, $n_D^{99\cdot6}$ 1·46205, $n_\beta^{99\cdot6}$ 1·46910. Ethyl tropane-2-carboxylate has $d_4^{20\cdot5}$ 1·0408, $n_\alpha^{20\cdot5}$ 1·47272, $n_D^{20\cdot5}$ 1·47562, $n_\beta^{20\cdot5}$ 1·48197, $n_\gamma^{20\cdot5}$ 1·48719, d_4^{15} 1·0468, n_α^{15} 1·47583, n_D^{15} 1·47805, n_β^{15} 1·48448, n_γ^{15} 1·48968. The methyl ester of *l*-ecgonine has $d_4^{20\cdot5}$ 1·1468, $n_\alpha^{20\cdot5}$ 1·48474, $n_D^{20\cdot5}$ 1·48765. Ethyl tropidine-2-carboxylate has $d_4^{21\cdot3}$ 1·0625, $n_\alpha^{21\cdot3}$ 1·49173, $n_D^{21\cdot3}$ 1·49480, $n_\beta^{21\cdot3}$ 1·50300, $d_4^{11\cdot7}$ 1·0721, $n_\alpha^{11\cdot7}$ 1·49615, $n_D^{11\cdot7}$ 1·49930, $n_\beta^{11\cdot7}$ 1·50768, $n_\gamma^{11\cdot7}$ 1·51462. Ethyl tropinone-2-carboxylate has $d_4^{20\cdot8}$ 1·1207, $n_\alpha^{20\cdot8}$ 1·49225, $n_D^{20\cdot8}$ 1·49537, $n_\beta^{20\cdot8}$ 1·50432, $d_4^{18\cdot7}$ 1·1228, $n_\alpha^{18\cdot7}$ 1·49312, $n_D^{18\cdot7}$ 1·49626, $n_\beta^{18\cdot7}$ 1·50353. Tropacocaine has $d_4^{100\cdot1}$ 1·0426, $n_\alpha^{100\cdot1}$ 1·50440, $n_D^{100\cdot1}$ 1·50801, $n_\beta^{100\cdot1}$ 1·51840, $n_\gamma^{100\cdot1}$ 1·52707. *d*-ψ-Cocaine has $d_4^{99\cdot6}$ 1·1020, $n_\alpha^{99\cdot6}$ 1·49862, $n_D^{99\cdot6}$ 1·50218, $n_\beta^{99\cdot6}$ 1·51199, $n_\gamma^{99\cdot6}$ 1·51959. $(d+l)$-ψ-Cocaine has $d_4^{99\cdot5}$ 1·1026, $n_\alpha^{99\cdot5}$ 1·49867, $n_D^{99\cdot5}$ 1·50209, $n_\beta^{99\cdot5}$ 1·51193, $n_\gamma^{99\cdot5}$ 1·51996. ψ-Pelletierine has $d_4^{99\cdot5}$ 1·0014, $n_\alpha^{99\cdot5}$ 1·47351, $n_D^{99\cdot5}$ 1·47596, $n_\beta^{99\cdot5}$ 1·48289, $n_\gamma^{99\cdot5}$ 1·48861. Ethyl *N*-methylpyrrolidine-2 : 5-diacetate has $d_4^{15\cdot4}$ 1·0490, $n_\alpha^{15\cdot4}$ 1·45872, $n_D^{15\cdot4}$ 1·46113, $n_\beta^{15\cdot4}$ 1·46765, $n_\gamma^{15\cdot4}$ 1·47035.

s-Copellidine has $d_4^{19\cdot0}$ 0·8315, $n_\alpha^{19\cdot0}$ 1·44113, $n_D^{19\cdot0}$ 1·44354, $n_\beta^{19\cdot0}$ 1·44982, $n_\gamma^{19\cdot0}$ 1·45524, and is converted by the action of methyl iodide into N-*methyl*-2 : 4 : 6-*trimethylpiperidine*, a colourless oil, which has b. p. 153—155°, $d_4^{19\cdot7}$ 0·8231, $n_\alpha^{19\cdot7}$ 1·44063, $n_D^{19\cdot7}$ 1·44299, $n_\beta^{19\cdot7}$ 1·44952, $n_\gamma^{19\cdot7}$ 1·45471. *N*-Methyltetrahydroquinoline has $d_4^{17\cdot3}$ 1·0236, $n_\alpha^{17\cdot3}$ 1·57620, $n_D^{17\cdot3}$ 1·58268, $n_\beta^{17\cdot3}$ 1·60057. Bornyl acetate has $d_4^{22\cdot6}$ 0·9833, $n_\alpha^{22\cdot6}$ 1·45998, $n_D^{22\cdot6}$ 1·46225, $n_\beta^{22\cdot6}$ 1·46827, $n_\gamma^{22\cdot6}$ 1·47319. *iso*Bornyl acetate has $d_4^{23\cdot4}$ 0·9807, $n_\alpha^{23\cdot4}$ 1·45978, $n_D^{23\cdot4}$ 1·46191, $n_\beta^{23\cdot4}$ 1·46798, $n_\gamma^{23\cdot4}$ 1·47275. Bornyl *iso*valerate has $d_4^{22\cdot2}$ 0·9487, $n_\alpha^{22\cdot2}$ 1·45779, $n_D^{22\cdot2}$ 1·46001, $n_\beta^{22\cdot2}$ 1·46590, $n_\gamma^{22\cdot2}$ 1·47068. Camphidine reacts readily with methyl iodide, giving N-*methylcamphidine*, a colourless oil, which gives a *picrate*, short, slender needles, m. p. 234°; it has b. p. 195—197°, $d_4^{19\cdot0}$ 0·9011, $n_\alpha^{19\cdot0}$ 1·47378, $n_D^{19\cdot0}$ 1·47625, $n_\beta^{19\cdot0}$ 1·48308, $n_\gamma^{19\cdot0}$ 1·48869, $d_4^{20\cdot8}$ 0·8998, $n_\alpha^{20\cdot8}$ 1·47311, $n_D^{20\cdot8}$ 1·47552, $n_\beta^{20\cdot8}$ 1·48230, $n_\gamma^{20\cdot8}$ 1·48767.

It is concluded that, in general, a molecule containing a seven- or eight-membered ring having a –NMe– group as a bridge, shows a depression in the values of the molecular refraction and molecular dispersion. W. S. N.

Spectrochemistry of Compounds with Augmented Conjugations. K. von Auwers (*J. prakt. Chem.*, 1923, [ii], 105, 361—384).—The following data are recorded and discussed. [With H. Westermann.]—Allylpropenylcarbinol,

$CH_2:CH\cdot CH_2\cdot CH(OH)\cdot CH:CHMe$,

has b. p. 61—62°/15 mm., d_4^{20} 0·8612, n_α^{20} 1·45089, n_{He}^{20} 1·45414, n_β^{20} 1·46191, n_γ^{20} 1·46840, and gives, when distilled with potassium hydrogen sulphate in a current of hydrogen, $\Delta^{\alpha,\gamma,\epsilon}$-heptatriene, which has b. p. 113—114°, $d_4^{19\cdot8}$ 0·7636 (hence d_4^{20} 0·764), $n_\alpha^{19\cdot8}$ 1·50786, $n_{He}^{19\cdot8}$ 1·51604, $n_\beta^{19\cdot8}$ 1·53754, $n_\gamma^{19\cdot8}$ 1·55742, n_{He}^{20} 1·5160 (cf. Enklaar, A., 1913, i, 243).

[With J. Heyna.]—*Ethyl* β-*vinylacrylate* is prepared by the action of ethyl iodide on an ethereal solution of silver β-vinylacrylate; it polymerises very readily, and has b. p. 70—71°/31 mm., 59·9°/18 mm., or 57·2—57·5°/13 mm., $d_4^{22\cdot9}$ 0·9348, $n_\alpha^{22\cdot9}$ 1·46948, $n_{He}^{22\cdot9}$ 1·47504, $n_\beta^{22\cdot9}$ 1·48928, $n_\gamma^{22\cdot9}$ 1·50252, n_{He}^{20} 1·4764. Closely corresponding figures for *d* and *n* are quoted for other temperatures. Ethyl sorbate has b. p. 81°/15 mm., or 76·5°/12 mm., $d_4^{15\cdot25}$ 0·9405, $d_{20}^{14\cdot85}$ 0·9408, $n_\alpha^{15\cdot25}$ 1·49149, $n_{He}^{15\cdot25}$ 1·49775, $n_\beta^{15\cdot25}$ 1·51395, n_{He}^{20} 1·4956. Ethyl α-methylsorbate has $d_4^{16\cdot5}$ 0·9501 (d_4^{20} 0·947), $n_\alpha^{16\cdot5}$ 1·49306, $n_{He}^{16\cdot5}$ 1·49907, $n_\beta^{16\cdot5}$ 1·51492, $n_\gamma^{16\cdot5}$ 1·52998, n_{He}^{20} 1·4976. Ethyl α-ethylsorbate has $d_4^{15\cdot3}$ 0·9345 (d_4^{20} 0·931), $n_\alpha^{15\cdot3}$ 1·49076, $n_{He}^{15\cdot3}$ 1·49653, $n_\beta^{15\cdot3}$ 1·51162, $n_\gamma^{15\cdot3}$ 1·52605, n_{He}^{20} 1·4944. Ethyl γ-methylsorbate has $d_4^{15\cdot6}$ 0·9499 (d_4^{20} 0·946), $n_\alpha^{15\cdot6}$ 1·49484, $n_{He}^{15\cdot6}$ 1·50087, $n_\beta^{15\cdot6}$ 1·51642, $n_\gamma^{15\cdot6}$ 1·53138, n_{He}^{20} 1·4989. Ethyl βδ-dimethylsorbate has $d_4^{18\cdot5}$ 0·9343 (d_4^{20} 0·933), $n_\alpha^{18\cdot5}$ 1·48301, $n_{He}^{18\cdot5}$ 1·48823, $n_\beta^{18\cdot5}$ 1·50175, $n_\gamma^{18\cdot5}$ 1·51447, n_{He}^{20} 1·4876. Diethyl crotonylidenemalonate has b. p. 149°/15 mm., $d_4^{14\cdot3}$ 1·0508 (d_4^{20} 1·045), $n_\alpha^{14\cdot3}$ 1·47867, $n_{He}^{14\cdot3}$ 1·48353, $n_\beta^{14\cdot3}$ 1·49629, n_{He}^{20} 1·4809.

Sorbyl chloride has $d_4^{18\cdot75}$ 1·0666 (d_4^{20} 1·065), $n_\alpha^{18\cdot75}$ 1·54707, $n_{He}^{18\cdot75}$ 1·55710, $n_\beta^{18\cdot75}$ 1·58453, n_{He}^{20} 1·5566.

[With W. MÜLLER.]—The ethyl ester of the stable cinnamylideneacetic acid (Vorländer, A., 1906, i, 362), has m. p. 25—26°, $d_4^{41\cdot6}$ 1·0299 ($d_4^{42\cdot2}$ 1·0294, d_4^{20} 1·049), $n_\alpha^{42\cdot2}$ 1·60039, $n_{He}^{42\cdot2}$ 1·61348, $n_\beta^{42\cdot2}$ 1·65080, $n_\gamma^{42\cdot2}$ 1·69311, n_{He}^{20} 1·6233. *Ethyl* allo*cinnamylideneacetate* is a colourless, mobile oil, which decomposes when heated under 10 mm. pressure. It has $d_4^{16\cdot8}$ 1·0473 (d_4^{20} 1·044), $n_\alpha^{16\cdot8}$ 1·60645, $n_{He}^{16\cdot8}$ 1·61950, $n_\beta^{16\cdot8}$ 1·65722, $n_\gamma^{16\cdot8}$ 1·70002, n_{He}^{20} 1·6181. *Ethyl α-methylcinnamylidene acetate* is an oil which cannot be distilled. It has d_4^{22} 1·0391 (d_4^{20} 1·041), n_α^{22} 1·60324, n_{He}^{22} 1·61641, n_β^{22} 1·65401, n_{He}^{20} 1·6155. β-Methylcinnamylideneacetic acid has m. p. 156—157° (Kohler, A., 1910, i, 484, gives m. p. 153°); its *ethyl* ester is an oil, which cannot be distilled, and has $d_4^{25\cdot1}$ 1·0384 (d_4^{20} 1·043), $n_\alpha^{25\cdot1}$ 1·58849, $n_{He}^{25\cdot1}$ 1·59936, $n_\beta^{25\cdot1}$ 1·63013, $n_\gamma^{25\cdot1}$ 1·66379, n_{He}^{20} 1·6017. γ-*Methylcinnamylideneacetic acid*, short, thick prisms, m. p. 108—110°, is prepared by the condensation of malonic acid with α-methylcinnamic acid in the presence of hot pyridine, which is accompanied by elimination of carbon dioxide, or by dehydrating the hydroxy-ester formed by condensing α-methylcinnamic acid, ethyl bromoacetate, and zinc in benzene solution. *Ethyl γ-methylcinnamylideneacetate*, a colourless oil, which cannot be distilled, has $d_4^{20\cdot3}$ 1·0387 (d_4^{20} 1·039), $n_\alpha^{20\cdot3}$ 1·59010, $n_{He}^{20\cdot3}$ 1·60100, $n_\beta^{20\cdot3}$ 1·63176, $n_\gamma^{20\cdot3}$ 1·66551, n_{He}^{20} 1·6012. Ethyl β-acetylacrylate has $d_4^{18\cdot1}$ 1·0387 (d_4^{20} 1·037), $n_\alpha^{18\cdot1}$ 1·44987, $n_{He}^{18\cdot1}$ 1·45346, $n_\beta^{18\cdot1}$ 1·46250, $n_\gamma^{18\cdot1}$ 1·47081, n_{He}^{20} 1·4526. Ethyl muconate has $d_4^{98\cdot8}$ 0·9832 ($d_4^{99\cdot1}$ 0·9829), $n_\alpha^{99\cdot1}$ 1·46178, $n_{He}^{99\cdot1}$ 1·46755, $n_\beta^{99\cdot1}$ 1·48259, $n_\gamma^{99\cdot1}$ 1·49695. Dimethyl β-methyl-$\Delta^{\alpha\gamma}$-butene-αδ-dicarboxylate has $d_4^{34\cdot8}$ 1·1006 ($d_4^{34\cdot9}$ 1·1005, d_4^{20} 1·115), $n_\alpha^{34\cdot9}$ 1·50142, $n_{He}^{34\cdot9}$ 1·50762, $n_\beta^{34\cdot9}$ 1·52413, $n_\gamma^{34\cdot9}$ 1·53993, n_{He}^{20} 1·5143. The corresponding diethyl ester has b. p. 163—164°/19 mm. (Stephen and Weizmann, T., 1913, **103**, 276, give b. p. 170°/10 mm.), and does not solidify when strongly cooled. It has d_4^{17} 1·0586 (d_4^{20} 1·056), n_α^{17} 1·49515, n_{He}^{17} 1·50081, n_β^{17} 1·51560, n_γ^{17} 1·52985, n_{He}^{20} 1·4995.

W. S. N.

Dispersion Accompanying Magnetic Double-refraction. G. SZIVESSY (*Z. Physik*, 1923, **18**, 97—104).—Values of the phase difference, ψ, between the ordinary and extraordinary rays propagated in a magnetic field of strength $H=10{,}100$ gauss, and of the respective refractive indices n, at about 20° are tabulated for λλ 486, 520, 550, 589, 620, and 656 μμ in the cases of toluene, *p*-xylene, *m*-xylene, chlorobenzene, bromobenzene, quinoline, anethole, benzoyl chloride, benzyl alcohol, and benzonitrile. From the results the respective values of the Cotton-Mouton constant, C, and the Havelock constant, h, are calculated by means of the equations $\psi=ClH^2$ and $C=h(n^2-1)^2/n\lambda$, where l denotes the length of path traversed in the respective substances. In the case of any of the substances investigated, the respective values of h are found to be independent of the wave-length employed, in accordance with Havelock's theory.

J. S. G. T.

The Influence of Foreign Gases on the Secondary Spectrum of Hydrogen. S. BARRATT (*Phil. Mag.*, 1923, [vi], **46**, 627—629).—In continuation of previous work on the enhancement of lines in the secondary spectrum of hydrogen due to the presence of helium (A., 1922, ii, 461), the author finds that similar changes, evidently related although on a far smaller scale, are produced by argon, whilst oxygen exerts no influence of the kind. The secondary hydrogen lines λλ, 6392·99 and 6111·08 Å., previously observed only in the presence of helium, were developed when argon was present.
J. S. G. T.

The Zeeman Effect associated with the Red and Blue Hydrogen Lines. K. FÖRSTERLING and G. HANSEN (*Z. Physik*, 1923, **18**, 26—33).—In a magnetic field of strength up to 20,000 gauss, each component of the doublets H_α and H_β in the hydrogen spectrum becomes a normal Zeeman triplet. Contrary to the conclusion of Erochin (*Ann. Physik*, 1913, [iv], **42**, 1054), the authors find that the central components of each pair of triplets arising respectively from H_α and H_β are displaced towards one another in the magnetic field, a result which is not in accord with any current theory of the Zeeman effect. J. S. G. T.

Ultra-violet Resonance Spectra of Iodine Vapour. OTTO OLDENBERG (*Z. Physik*, 1923, **18**, 1—11).—Iodine vapour, excited by ultra-violet radiation of short wave-length emits a resonance spectrum comprising a series of lines characterised by the same regularity and nuclear vibration quanta as in the case of the resonance spectrum excited by the green mercury line. In the neighbourhood of the band λ 3250 Å., additional bands λλ 3169, 3191, 3212, 3237, 3261, 3285, 3311, 3338, 3364, 3394, 3417, 3442, 3466, 3495, 3495, 3525, 3559, 3596, 3640, 3680, 3720, 3765, 3813, 3866, 3925, and 4007 Å. are observed when extraneous light is carefully excluded. The frequencies, ν, of about thirty-five lines conforming with Stokes's law, and of three lines of shorter wave than that of the exciting radiation, are, in the case of excitation with the zinc line λ 1900, represented by the equation $\nu=52630(1-0\cdot00416n+0\cdot000017n^2)$, $n=0, 1, 2, 3. \ldots$ Toward the region of long wave-lengths, the resonance spectrum passes gradually into the ultra-violet fluorescence band spectrum of iodine vapour observed by McLennan (A., 1913, ii, 455; 1914, ii, 829), which corresponds fairly well with the ultra-violet bands in the spectrum emitted by iodine vapour under electrical excitation. It is concluded that the band spectrum is the long wave-length extension of the short wave-length resonance spectrum. The author discusses a possible origin of emission of the fluorescence spectrum, which is excited only by radiation of wave-length shorter than 1950 Å. It is shown conclusively, in agreement with McLennan's result, that the visible and ultra-violet fluorescence spectra are emitted by the iodine molecule and are not attributable to the presence of an impurity. J. S. G. T.

Series Spectra in Oxygen and Sulphur. J. J. HOPFIELD (*Nature*, 1923, **112**, 437—438).—The series for oxygen previously

reported (*Physical Rev.*, 1923, **21**, 710) have been extended from two to seven and from one to six members, respectively. No second member of the third series was found. Gaseous sulphur dioxide has a strong absorption band extending from λ 2500 to λ 1700, and another from λ 1650 indefinitely into the ultra-violet. The spark spectrum of sulphur extends to λ 350; the arc spectrum contains a number of triplets of wide separation and constant frequency difference which have been classified in series by analogy with oxygen. In the cases of both oxygen and sulphur, the intensities and separations observed are inverted as compared with the known spectra of these elements in the visible and ultra-red. One stable and two metastable forms of each of the elements atomic oxygen and atomic sulphur appear to exist. The resonance and ionising potentials, respectively, for the stable forms are calculated to be: oxygen, 9·11 and 13·56 volts; sulphur, 6·50 and 10·31 volts.

A. A. E.

The Carbon Arc Spectrum in the Extreme Ultra-violet. II. F. SIMEON (*Proc. Roy. Soc.*, 1923, [*A*], **104**, 368—375).—In continuation of previous work (this vol., ii, 45), the author has shown that the spectrum of the carbon arc in vacuum extends as far in the extreme ultra-violet as that of the spark, with the exception of a very faint line at λ 360·5 Å. The wave-lengths and relative intensities of twenty-five new lines in the region between λ 976·7 and λ 371·5 Å. are tabulated. In agreement with a deduction from the quantum theory, it is found that a potential of between 30 and 40 volts is sufficient to excite the *L*-series of carbon lines. Reasons are advanced for attributing the lines λλ 1751·8, 1760·6, 2297·1, 2509·5, and 2512·4 Å., excited at 30 volts to the carbon spark spectrum, and the remainder to the arc spectrum. J. S. G. T.

Structure of the Spectrum of Neon. A. LANDÉ (*Z. Physik*, 1923, **17**, 292—294).—It is shown that certain lines in the neon spectrum analysed by Paschen (A., 1920, ii, 69, 718), which, according to Grotrian (A., 1922, ii, 179) may be regarded as L_1 and L_2 terms derived by extrapolation of the *L*-series of doublets in the Röntgen spectrum of neon, can be classified as the first components of a system of quintuplets, two systems of triplets, and a system of singlets. In the latter classification, both L_1 and L_2 terms originate by the displacement of electrons from 2_2 orbits. J. S. G. T.

Excitation of the Spark Spectra of Lithium. E. VON ANGERER (*Z. Physik*, 1923, **18**, 113—119).—The literature of the excitation of spark spectra is briefly reviewed, and experimental details of attempts made by the author to excite the spectra of Li^{II} and Li^{III} are given. The following lines, hitherto unrecorded, and possibly attributable to Li^{II}, were observed in the vacuum spectrum: 3143·7, 3028·5, 3024·6, 2988·5, 2959·5, 2899·66, 2869·90, 2866·45, 2704·60, 2635·20. J. S. G. T.

Spectra and the Periodic Classification. M. A. CATALÁN (*Anal. Fís. Quím.*, 1923, **21**, 321—329; cf. this vol., ii, 104, 105, 356).—Further data are given for the spectrum of manganese. The

relation of ionisation potentials to the periodic classification is discussed. Well defined maxima are shown for zinc and cadmium and a less marked maximum for calcium. G. W. R.

The α-Lines in the *K*-Series Tungsten Spectrum. CHARLES CROFUTT (*Proc. Iowa Acad. Sci.*, 1921, **28**, 117—118; cf. Duane and Shimizu, *Physical Rev.*, 1919, **13**, 306; Duane and Patterson, A., 1921, ii, 363; *Proc. Nat. Acad. Sci.*, 1920, **6**, 509; Duane and Stenström, *ibid.*, 1920, **6**, 477).—Experiments with a crystal of thickness 0·015 cm., a front slit 0·005 cm. wide, and a prolonged exposure did not reveal the α_3-line, which is therefore assumed to have an intensity less than one-tenth of that of the α_2-line, or to differ from it in wave-length by less than 0·05%.

CHEMICAL ABSTRACTS.

The Absorption Spectra of some Metallic Vapours. WALTER GROTRIAN (*Z. Physik*, 1923, **18**, 169—182).—In continuation of previous work (this vol., ii, 106), the author has investigated the absorption of visible radiation and radiation extending into the ultra-violet as far as about λ 2350 Å. by the vapours of copper, silver, gallium, lead, tin, bismuth, antimony, and manganese. In the case of copper vapour, in a tube 30 cm. long, absorption of the first members of the doublet principal series, λλ 3247 and 3274 Å., was observed at about 1050°. Under similar conditions, absorption of the corresponding lines λλ 3280 and 3383 Å. in the case of silver vapour was observed at about 900°. In the case of gallium, absorption of the first members of the subordinate series was observed at 850° in the case of the $2p_2$-lines λλ 2874 and 4033 Å., whilst in the case of the $2p_1$ lines λλ 2943·7, 2944·2, and 4172 Å. absorption was first observed at about 900°. Absorption of the line λ 2833 Å. by 30 cm. of lead vapour was observed at 550°. At temperatures above 950°, the line broadened unsymmetrically, the centre being displaced towards the red end of the spectrum. At 1200°, a continuous absorption band, about 10 Å. wide, relatively sharply defined towards the blue and indefinite towards the red end of the spectrum, was observed. The broadening is attributable to the formation of lead molecules, probably Pb_2. From the position of the line 2833 in the series proposed for the lead spectrum by Thorsen (*Naturwiss.*, 1923, **11**, 78), the ionisation potential of the lead atom is found to be 7·38 volts. As the normal condition of the lead atom corresponds with a *p*-term, it is concluded that the 82 electrons associated with the atom are arranged in a 6_2 orbit. Absorption of other lines was observed at higher temperatures, in accordance with theoretical considerations. The partial pressure of the atoms exhibiting absorption was of the order 10^{-5} mm. In a tube 15 cm. long, absorption of the lines λλ 3009·2, 2863·4, and 2706·6 Å. by tin vapour was observed at 1,050°. Bismuth exhibited typical absorption of the line 3067 Å. at 650°. At higher temperatures, bands were strongly developed. It is suggested that the molecule of bismuth vapour is partly polyatomic. Absorption of the manganese triplet 2794·82, 2798·27, and 2801·07 by manganese vapour was observed at about 850°, whilst absorption of the triplet 4030·76,

4033·07, and 4034·49 occurred at about 880°. The results are considered to justify the assumption by Catalán (A., 1922, ii, 726) of the $1S$ term as the normal condition of the manganese atom.

J. S. G. T.

Röntgen Spectroscopy. Absorption Spectra in the *L*-Series Relating to the Elements from Lanthanum (57) to Hafnium (72). D. COSTER, Y. NISHINA, and S. WERNER (*Z. Physik*, 1923, **18**, 207—211).—The authors have determined the respective wave-lengths of the heads of absorption bands L_I, L_{II}, and L_{III} in the L-series relating to the elements of atomic numbers 57, 58, 64, and 68 to 72. The results confirm the existence, suggested by Bohr and Coster (this vol., ii, 110) of an anomaly in the level curves in the region of the rare earths. J. S. G. T.

Influence of the Aperture of the Spectrometric Slit on the Form of the Absorption Curves of the Infra-red. G. B. BONINO (*Gazzetta*, 1923, **53**, 591—597).—A mathematical paper which does not lend itself to abstraction. T. H. P.

Spectrochemistry in the Ultra-red. G. B. BONINO (*Gazzetta*, 1923, **53**, 555—575).—The author gives a summary of previous publications on this subject and describes the apparatus and methods of observation employed in his own investigations (see succeeding abstracts). T. H. P.

Spectrochemistry in the Ultra-red. II. Absorption of the Alcohols. G. B. BONINO (*Gazzetta*, 1923, **53**, 575—582; cf. preceding abstract).—From the results of investigations on the absorption of alcohols in the ultra-red region between 2·5 and 3·8 μ, Henri and Wurmser (Henri, "Études de Photochimie," 1919, 45) deduced a linear relation between the molecular coefficient of maximum absorption and the chemical composition. The author finds, however, that, if the slit of the spectrometer used is gradually made narrower, the absorption curves of the alcohols are not so simple as is represented by Henri and Wurmser's results, the value of which is questionable.

Compounds containing hydrogen united to a single other element exhibit in the ultra-red a simple absorption band of constant spectral position under ordinary dispersive conditions, whereas compounds containing hydrogen atoms united to two different elements present, in the same region of the spectrum, two distinct bands. In the case of the alcohols, the maximum of one of these bands coincides with that shown by the hydrocarbons, and that of the other with the maximum of the band exhibited by water. It appears, then, that the position of the maximum for these bands is to be attributed to the hydrogen and varies, in one and the same spectral region, according to the nature of the linking (cf. Puccianti, A., 1900, ii, 585).

On the assumption that the bands in question are to be attributed to the partial field of the valency electron of the hydrogen (cf. Stark, "Prinzipien der Atomdynamik," 1915), Planck's elementary law, $h\nu=E$, where ν is an infra-red frequency, h Planck's constant, and E the energy of the field or a measure of the work necessary to

rupture the bond between the valency electron of the hydrogen and the other atom, indicates that the frequency ν should be proportional to the energy value of the bond. With hydrofluoric, hydrochloric, and hydrobromic acids the author finds that this is very nearly the case. Moreover, Haber's relation, $\nu_{uv}/\nu_{ir}=\sqrt{M}/m$, where ν_{uv} and ν_{ir} are, respectively, the ultra-violet and infra-red characteristic frequencies, m the mass of the electron, and M that of the vibrating atom, is found to hold satisfactorily for the hydrocarbons if the mass of the hydrogen atom is put in place of M and the total mass of the electrons forming the bond of Stark's hypothesis in place of m.

With different compounds, the molecular absorption coefficient for the band in the infra-red varies in the same sense as the number of hydrogen atoms in the molecule, and in a homologous series the coefficient of maximum absorption varies, approximately and with certain limitations, proportionally with the number of hydrogen atoms in the molecule. It may thus be assumed that $d\epsilon = Kd\rho/\rho$, where ρ is the ratio between the numbers of hydrogen atoms and molecules present, K a constant, and ϵ the coefficient of absorption divided by the number of g.-mols. present. Integration of this expression between two limits corresponding with the ratios of two definite homologous compounds having, respectively, n_1 and n_2 molecules of hydrogen per molecule yields, $\epsilon_2=\epsilon_1+C\log_{10}.\ n_2/n_1$. Thus from the value of ϵ for one compound that of a homologous compound can be calculated. Excellent agreement is obtained in this way with the lower monohydric aliphatic alcohols and with certain higher members of the ethylene series. T. H. P.

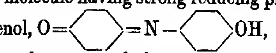
Spectrochemistry in the Ultra-red. III. Absorption of certain Solutions. G. B. Bonino (*Gazzetta*, 1923, **53**, 583—590; cf. preceding abstracts).—The author has investigated the molecular coefficient of infra-red absorption ϵ of solutions of methyl alcohol in carbon tetrachloride under dispersion conditions analogous to those of Henri's experiments ("Études de Photochimie," 1919), the values of ϵ being calculated by means of the expression $I=I_0 10^{-\epsilon cd}$, in which c is the number of g.-mols. of the substance per litre of the liquid examined, d the thickness of the liquid layer in cms., and I_0 and I the respective intensities of the radiation emerging from the cell charged with the solvent and the solution. The results obtained show that the value of ϵ increases with the dilution of the alcohol.

The case of the alcohols being complicated by the appearance in the infra-red spectrum of a double band with maxima presumably attributable to the hydroxyl group and the hydrogen united with carbon, similar measurements have been made on benzene and its solutions in carbon tetrachloride. Here, too, the molecular coefficient for the position of maximum absorption increases with the dilution of the benzene. Both in this instance, and also with the carbon tetrachloride solutions of methyl alcohol, the curve connecting the logarithm of the molecular absorption coefficient with the logarithm of the volume in litres of solution containing 1 g. mol. of the solute is sensibly linear at relatively high concentrations,

but at lower concentrations a constant value of the former logarithm is approached. For the benzene solutions, especially the more dilute ones, the experimental values are in moderately good agreement with those calculated from the expression given by Baly and Tryhorn (A., 1916, ii, 278). T. H. P.

The Absorption Spectra of the Vapours and Solutions of Various Ketones and Aldéhydes. JOHN EDWARD PURVIS (T., 1923, **123**, 2515—2521).

Absorption Spectra and Molecular Phases. I. RICHARD ALAN MORTON and HARRY BARNES (T., 1923, **123**, 2570—2572).

A Theory of Colour Production. I and II. JULIUS STIEGLITZ (*Proc. Nat. Acad. Sci.*, 1923, 9, 303—308, 308—312).—I. All organic dyes have the property of being reducible to a so-called leuco-compound which can in turn be oxidised again to the dye. Fundamentally, oxidation consists in the removal of electrons from an atom, through which process it acquires the power of attracting electrons. The author traces colour production in dyes to electronic vibrations brought about by the oxidising power of an oxidised atom exerting its influence on a neighbouring atom in the molecule having strong reducing properties. In the case of indophenol,  which exemplifies the theory, the carbon atom of the quinonoid nucleus attached to the nitrogen atom is fully oxidised and consequently has a strong attraction for the electrons attached to the corresponding carbon atom in the strongly reducing phenolic nucleus. These electrons, being "largely freed from intra-atomic restraints," have their vibrational orbits so modified that absorption of white light results. The known fact that the reducing power of organic compounds such as quinol or *p*-aminophenol is greatly increased by strong bases can be correlated with the deepening effect of such bases on the colour of indophenol. Similarly, the fact that basic dyes such as pararosaniline have their maximum colour depth and intensity when combined with acid may be due to the known effect of acids in intensifying the oxidising power of oxidising agents. The electronic vibrations postulated must be intra-atomic, and must not involve any actual transference of electrons from one atom to another, as this would involve the migration of the hydrogen atom of the hydroxyl group in indophenol from one nucleus to the other. There is positive evidence that such migration does not take place in the dimethylmurexides, of which two can be prepared. The one is prepared from dimethyluramil and alloxan, the other from uramil and dimethylalloxan, and in both cases the original components can be recovered by decomposition of the dye. The source of colour cannot therefore be migration of the electrons, as this would, in the case under consideration, involve migration of the methyl groups.

II. The ideas developed in the preceding section are applied to inorganic compounds, and it is concluded that colour in these compounds must be ascribed to intra-atomic or inter-atomic oxida-

tion-reduction potentials of sufficient force to make possible vibrations of electrons in the reducing component long enough to absorb visible light waves. Combination of a strong oxidising kation with a strong reducing anion leads to strong colour, as in PtI_4. In permanganates and chromates the source of colour lies in the tendency of the valence electrons of the oxide oxygen atoms to pass to the strongly oxidising atoms $Mn^{+++}_{+++}{}^{+}$ and Cr^{+++}_{+++}. Intense colour is produced by the association of atoms of a given element in two conditions of oxidation, as in ferrosoferric oxide, ferrous ferricyanide, and red lead. The colour of chromic salts must be due to intra-atomic forces caused by the presence in the atom Cr^{+++} of three valence electrons. Aluminium and gallium salts contain no such valence electrons and are colourless. A number of other examples are discussed. E. H. R

Röntgenographic Investigations of Systems Capable of Luminescence. ARTHUR SCHLEEDE and HANS GANTZCKOW *Z. physikal. Chem.*, 1923, **106**, 37—48).—Substances capable of phosphorescence are considered, and it is shown that the power of luminescence is never connected with glass-like substances, but only with crystalline substances, provided that a few of the metallic atoms of the fundamental substance are replaced by atoms which are foreign to the lattice of the fundamental substance. The various types of luminescence phenomena, cathodic luminescence, fluorescence, phosphorescence, in one and the same fundamental substance prepared in various ways, depend in all probability on various conditions of deformation of the lattice. J. F. S.

Radiochemistry and Fluorescence. JEAN PERRIN (*Compt. rend.*, 1923, **177**, 612—618).—The author re-discusses previous ideas on the radiation theory of chemical change (cf. A., 1922, ii, 628), more particularly in connexion with the recent work of Levaillant (this vol., ii, 597). The rate of decolorisation of new methylene-blue and fluorescent-blue in glycerol solution is appreciably increased by rise in temperature. Thus, for the former blue, at temperatures from 19—55°, the velocity of disappearance of colour under the influence of orange rays is multiplied by 1·3 for an increase, by one-thirtieth, of the absolute temperature. From this, the author concludes that the infra-red rays producing the critical molecules of glycerol (the cause of the reduction of the colouring matter) have a frequency of 5×10^{13} and a wave-length of 6μ. Fluorescent-blue gave similar results, but neither solution underwent change in absence of light. At 150°, however, New methylene-blue solutions are slightly decolorised in the dark.
E. E. T.

Luminescence of Organo-magnesium Halides. R. T. DUFFORD, S. CALVERT, and DOROTHY NIGHTINGALE (*J. Amer. Chem. Soc.*, 1923, **45**, 2058—2072).—An investigation of the luminescence of organo-magnesium halides. It is shown that Grignard reagents in ethereal solution exhibit chemi-luminescence on oxidation by oxygen only when the magnesium is attached to an unsaturated

carbon atom. This holds for both aromatic and aliphatic compounds in all the cases (60) investigated. The nature of the solvent affects the intensity of the luminescence but not the wave-length. Zinc and mercury organic halides give no luminescence. Both the intensity and the wave-lengths of the luminescence are affected by the nature of the reacting halogen. The wave-length and the intensity are affected by the nature of the organic radicle involved, and especially by the nature of the substituting groups in cyclic compounds. The effect depends on the position of the substituting group and its chemical character. But it is definitely shown that the mass of the substituting group' is not the controlling factor. Certain cases of very bright chemi-luminescence are described and that of magnesium *p*-chlorophenyl bromide is believed to be the brightest yet recorded. A new method of preparing chlorine-containing Grignard compounds is described; this consists in carrying out the Grignard reaction in *iso*amyl ether and using either iodine or ethyl bromide as catalyst. Many Grignard compounds emit light when treated with chloropicrin or with bromopicrin. This light is not the same as that emitted on oxidation with oxygen. Many Grignard compounds, and especially their oxidation products, are found to be fluorescent in ultra-violet light. Tables are given of the luminescent properties of sixty Grignard compounds. J. F. S.

Rotatory Polarisation in an Orthorhombic Crystal [Triphenylbismuthine Dichloride] Exhibiting Crossed Axial Dispersion. GILBERT GREENWOOD (*Min. Mag.*, 1923, **20**, 123—130).—Circular polarisation, if any, in optically biaxial crystals is masked by the double refraction, but when they exhibit crossed axial dispersion they are optically uniaxial for a certain colour, and the effects of the circular polarisation can then be observed in light of that colour. In crystals of triphenylbismuthine dichloride (orthorhombic-holoaxial class, $a:b:c=0{\cdot}774:1:0{\cdot}409$), the acute positive bisectrix is perpendicular to (010), and for red to green light the axial plane is (100), whilst for green to violet it is (001). For green light of wave-length 510 $\mu\mu$, the crystal is uniaxial at 17°. A section perpendicular to the acute bisectrix does not extinguish between crossed nicols in parallel white light, but transmits light of a bright green colour: this was examined spectroscopically. The optic axial angles for different wave-lengths were determined at two temperatures (17° and 35°). Similar phenomena are shown by potassium sodium tartrate. A salt of one part of sodium potassium tartrate and two parts of sodium ammonium tartrate is uniaxial in the green, whilst a salt of equal proportions is uniaxial in the blue. L. J. S.

Absorption and Anomalous Rotation Dispersion of Camphorquinone. NINA WEDENEEWA (*Ann. Physik*, 1923, **72**, 122—140).—Measurements of the rotation, the ellipticity, and the absorption of a solution of camphorquinone in toluene (0·6913 g. in 200 c.c.) have been made in the regions of the absorption bands. The results are discussed from the point of view of Drude's theory,

and the activity coefficients have been calculated. A method of measuring the phase difference and the dichroism is described.

J. F. S.

Models for the Illustration of some Propositions of the Rules of Symmetry in the Exposition of Stereochemistry. ERNST MOHR (*J. pr. Chem.*, 1922, [ii], **105**, 93—101).—The author describes paper or cardboard models by means of which various types of molecular symmetry may be demonstrated. The original does not lend itself to abstraction, and must be consulted for details.

W. S. N.

Specific Action of Luminous Rays of Various Colours in Photosynthesis. V. LUBIMENKO (*Compt. rend.*, 1923, **177**, 606—608).—For most plants, the amount of photosynthesis in red light (λ 760—600 $\mu\mu$), as measured by the carbon dioxide exchange, is greater than that in bluish-violet light (λ 480—400 $\mu\mu$), although with a few plants, accustomed to diffused daylight, photosynthesis is nearly as great in bluish-violet as in red light.

E. E. T.

Influence of Drying on Photochemical Reactions. HEINRICH TRAMM (*Z. physikal. Chem.*, 1923, **105**, 356—401).—An apparatus is described by means of which the purification and drying of gases may be carried out at the temperature of liquid air. No drying agents are used, and a degree of dryness greater than that represented by a pressure of water vapour less than 0·004 mm. is achieved. The photochemical formation of ozone, hydrogen chloride, sulphuryl chloride, and carbonyl chloride and the photochemical decomposition of hydrogen chloride, hydrogen bromide, and hydrogen iodide in the presence of various quantities of moisture have been investigated. It is shown that a highly desiccated mixture of hydrogen and chlorine free from oxygen does not combine to a measurable extent under the influence of light. A mixture of carbon monoxide and oxygen which has been dried to the point where it ceases to be explosive and at high temperatures reacts very sluggishly in the dark, when exposed to ultra-violet light exhibits the same velocity of reaction as a similar moist mixture. This shows that the reversal of the photo-decomposition of carbon dioxide by ultra-violet light in the presence of traces of moisture as demonstrated by Coehn and Sieper (A., 1916, ii, 281) is not due to an acceleration of the formation of carbon dioxide, but to a retardation of the decomposition. Traces of sulphur dioxide retarded the decomposition of carbon dioxide by ultra-violet light in exactly the same way as water. Against the assumption that the accelerating action of water vapour on the reaction between carbon monoxide and oxygen under the influence of heat is due to the formation of formic acid as an intermediate product, it is shown that mixtures of oxygen and formic acid do not explode, whilst an equivalent mixture of hydrogen, oxygen, and carbon monoxide does so. A mixture of hydrogen and oxygen so dry that it does not explode in a vessel heated to a red heat but only combines slowly when exposed to ultra-violet light reacts at exactly

the same rate as the undried mixture. The author has been unable to dry hydrogen chloride and ammonia to such an extent that they do not combine. J. F. S.

The Influence of Ultra-violet Radiation on the Reactivity of Halogen attached to the Nucleus in the Presence and Absence of Catalysts. K. W. ROSENMUND, K. LUXAT, and W. TIEDEMANN (*Ber.*, 1923, **56**, [*B*], 1950—1957).—The reactivity of halogen atoms attached to aromatic nuclei is greatly enhanced by ultra-violet radiation; this is more particularly the case when copper is present as catalyst. Thus, for example, the chlorine atom of *p*-chlorobenzoic acid is removed quantitatively when its solution in aqueous potassium hydroxide (35%) is boiled for six hours in the presence of copper and ultra-violet light. The enhanced reactivity appears to be due to the effect of the radiation on the organic molecule, and not on the catalyst. The reaction between halogen compounds and alkali hydroxides under these conditions does not lead smoothly to the expected hydroxy-compounds, but the process is well adapted to the production of ethers from halogen compounds and alkyloxides, and to that of acids from halogen compounds and cyanides: $C_6H_4Cl\cdot CO_2H + KCN + 2H_2O \longrightarrow KCl + NH_3 + C_6H_4(CO_2H)_2$. Copper precipitated in the solution appears to be more effective than Ullmann's copper powder or Piccard's copper (A., 1922, ii, 216).

The reactions are carried out in small flasks of clear silica exposed to the light of a Heraeus mercury lamp. The following examples are cited: phenyl *iso*amyl ether, b. p. 210—215°, from bromobenzene and sodium *iso*amyloxide; phenyl *n*-propyl ether, from bromobenzene and sodium *n*-propoxide; *p*-tolyl *iso*amyl ether, b. p. 232—235°, from *p*-bromotoluene and sodium *iso*amyloxide; *o*-tolyl *iso*amyl ether, b. p. 213°, from *o*-bromotoluene and sodium *iso*amyloxide; *p*-anisyl *iso*amyl ether, b. p. 234—237°, from *p*-bromoanisole and sodium *iso*amyloxide. α-Bromonaphthalene and sodium *iso*amyloxide unexpectedly yield naphthalene in almost quantitative yield.

Potassium *p*-chloro- or *p*-bromo-benzoate and potassium cyanide in aqueous solution, in the presence of cuprous cyanide, give terephthalic acid in 70% yield. *p*-Bromobenzenesulphonic acid yields *p*-sulphobenzoic acid (yield 75%), whilst *p*-bromotoluene-*o*-sulphonic acid is similarly transformed into the corresponding carboxylic acid.

The formation of nitriles from alkyl halides and potassium cyanide is appreciably facilitated by the presence of cuprous cyanide and ultra-violet light. H. W.

The Protective Action of Antioxidising Substances [Polyphenols] against Fading of Dyed Fibres in the Light. P. SISLEY (*Bull. Soc. chim.*, 1923, [iv], **33**, 1079—1081).—It is found that certain polyphenols exercise a protective action on some dyes on the fibre, in that the latter are rendered more stable to the action of light and, sometimes, of oxygen. It is not possible, however, to draw any general theoretical conclusions from the results observed,

because it is found that a polyphenol which protects one dye may even accelerate the fading of a closely related dye. Tannin, for instance, has a well-marked protective action on methylene-blue dyed on silk, but has practically no effect on auramine. Hydroxylamine sulphate, again, protects methylene-blue, but accelerates the fading of phloxine, whilst thiocarbamide protects the latter, but accelerates the fading of the rhodamines. H. H.

Some Biochemical Effects of Polarised Light. ELISABETH SIDNEY SEMMENS (*Chemistry and Industry*, 1923, **42**, 954).—The hydrolysis of starch in the mustard seed, and also of starch grains when acted on by diastase in vitro, is accelerated by exposure to plane polarised light. It is suggested that the influence of polarised light brings about some change in the starch granules prior to the rupture of the membrane. C. H. R.

Influence of the Wave-length on the Energy Change in Carbon Dioxide Assimilation. OTTO WARBURG and ERWIN NEGELEIN (*Z. physikal. Chem.*, 1923, **106**, 191—218).—Making use of the method previously described (A., 1922, i, 1097) for measuring the energy changes accompanying the assimilation of carbon dioxide, the authors have investigated the change in the following spectrum ranges: infra-red, 800—900 $\mu\mu$, red, 780—700 $\mu\mu$; 690—610 $\mu\mu$; yellow, 578 $\mu\mu$; green, 546 $\mu\mu$; blue, 436 $\mu\mu$, and ultra-violet, 366 $\mu\mu$. There is no decomposition of carbon dioxide in the infra-red region and the decomposition in the ultra-violet and the long wave red 780—700 $\mu\mu$ has proved to be unsuitable for quantitative experiments. The absorption coefficient of a methyl alcohol extract of the colouring matter of the alga *Chlorella* has been determined for the four spectral regions and it is found that the value is smallest for the green line (α=0·09), 1·8 times as large for the yellow, 9 times as large in the red, and 20 times as large in the blue. The assimilation experiments were carried out with *Chlorella* stems, and show that the yield in the carbon dioxide assimilation decreases with decreasing wave-length. No relationship between the yield and the wave-lengths of the absorption bands can be found; the yield in the red, a region of strong absorption, is greater than that in the green, a region of very weak absorption, whilst the yield of this is greater than that in the blue, the region of strongest absorption. J. F. S.

The Photoelectric Conductivity of Cinnabar. B. GUDDEN and R. POHL (*Z. Physik*, 1923, **18**, 199—206).—Whilst the results obtained by the authors (A., 1921, ii, 145; this vol., ii, 528) and by Rose (*Z. Physik*, 1920, **3**, 174) are in substantial agreement in regard to the spectral distribution of the photo-sensitivity of cinnabar, they exhibit differences greater than the possible experimental error. These differences are now attributed to differences in the experimental conditions—direction and intensity of illumination, voltage applied to the crystal—whereby the increased conductivity of the crystal when illumined originates in a primary or secondary effect, or a combination of both effects, produced by the incident

radiation. The current produced by the secondary effect arises in somewhat the same manner as ionisation in a gas is produced by collisions. In an electric field transverse to the direction of illumination, the secondary current constitutes a greater proportion of the total current than is the case in a longitudinal field. The same considerations are applied to the discussion of selective maxima of sensitivity exhibited more especially by powders in strong electric fields. The energy relations observed in connexion with the photo-sensitivity of cinnabar are held to support, in a general manner, the truth of the photo-chemical equivalence law.

J. S. G. T.

The Passage of Corpuscular Radiation through Matter, and Atomic Constitution. II. W. BOTHE (*Jahrb. Radioaktiv. Elektronik*, 1923, **20**, 46—84).—The literature of the scattering and absorption of α- and β-rays, and of the production of secondary radiation and of ionisation by the passage of these rays through matter is critically reviewed. J. S. G. T.

The Period of Protactinium. JOHN H. MENNIE (*Phil. Mag.*, 1923, [vi], **46**, 675—685).—From a comparison of the α-activities of ionium and protactinium, separated from several kilograms of uranyl nitrate, the author has found the average life period of protactinium to be 18,000 years, in substantial agreement with the period of half-change, 12,500 years, found by Hahn and Meitner (A., 1921, ii, 150). J. S. G. T.

Radioactive Disintegration Series and the Relation of Actinium to Uranium. A. S. RUSSELL (*Phil. Mag.*, 1923, [vi], **46**, 642—656).—Regarding a disintegration series as made up of three types of successive changes, the author deduces that there are probably only four such series which are independent, these corresponding, respectively, with the values 222, 221, 220, and 219 for the respective atomic weights of components of the series having an atomic number 86. Of these, the series 221 is new. The series 222, 220 refer, respectively, to the uranium and thorium series, and it is shown that series 219 is the actinium series. Simple empirical relations between the periods of substances related by the expulsion of at least four α-particles without the expulsion of separate β-particles, and of substances related by the expulsion of an α-particle followed by two β-particles in succession and then an α-particle are given. It is deduced that the actinium series originates from an isotope of uranium having an atomic weight 239 (actinuranium-I), present to the extent of about 5% in ordinary uranium. Estimates of the periods of the substances preceding protoactinium in this series are given. Radioactive isotopes are compared with those of inactive elements, and it is suggested that thallium and bismuth, in addition to isotopes of lead, may form end-products of radioactive series. J. S. G. T.

The Short-lived Radioactive Products of Uranium. WILLIAM GEORGE GUY and ALEXANDER SMITH RUSSELL (T., 1923, **123**, 2618—2631).

Long-range Particles from Radium Active Deposit. L. F. BATES and J. STANLEY ROGERS (*Nature*, 1923, **112**, 435—436; cf. Kirsch and Pettersson, this vol., ii, 675).—Radium active deposit, $B+C$, on a brass disk was found to emit particles with ranges in air (15°/760 mm.) of 9·3, 11·1, and 13·2 cm., respectively, as well as particles (presumably hydrogen particles) of range >18 cm., in quantities of 380, 126, 65, and 160, respectively, compared with 10^7 of α-rays of range 6·97 cm. It was ensured that the long-range particles were not produced by collisions of the 6·97 cm. α-particles with air molecules, or by excitation in the mica sheets; they appeared to be independent of the metal on which the deposit was formed. It is considered possible that Kirsch and Pettersson's (*loc. cit.*) 12, 13, and 10 cm. hydrogen particles are actually long-range α-particles emitted by the active deposit. A. A. E.

Method for Photographing the Disintegration of an Atom, and a New Type of Rays. WILLIAM D. HARKINS and R. W. RYAN (*J. Amer. Chem. Soc.*, 1923, **45**, 2095—2107).—The rarity of a collision between a fast helium nucleus (α-particle) and the nucleus of an atom in a gas through which it is passing increases greatly as the directness of the collision increases. In three cases the authors have obtained photographs which show the rebound of the α-particle, and taking account of the number of photographs obtained and the fact that the α-particle has passed through about 12 billion atoms in air, this alone indicates that the nucleus of an atom of nitrogen or oxygen is of the order of slightly more than 10^{-13} cm. in radius. A more accurate value can be obtained by a mathematical analysis of all of the deflections of the α-particle through smaller angles. In an ordinary collision, three tracks meet in a point, one for the particle before collision, and a second for the same particle after collision. Should the oxygen or nitrogen nucleus disintegrate, then at least four tracks should meet, the additional track being due to a fragment, such as an electron, a hydrogen, or a helium nucleus disrupted from the bombarded nucleus. The chance of such a disintegration increases rapidly with the directness of the collision and with the speed of the α-particle. The authors have obtained a photograph in which the fourth track appears, and this should characterise an atomic disintegration. That this track starts from the proper point in space is shown by two projections obtained simultaneously. These give two views at an angle of 90°. Rays of a new type, designated by the authors ζ-rays, have been photographed. In this case, the α-particle evidently drives particles from two widely separated atoms in its path. It is remarkable that the two tracks thus obtained lie in almost parallel planes, both are highly curved and almost parallel lines, and both have a sharp retrograde motion. It seems probable that the ζ-rays are due to electron emission. The particles must be very light, since the direction of the α-particle is not materially affected by the emission, and the tracks of the particles are moderately long, very much longer than those of the previously recorded δ-rays. The apparatus used by the authors

in this work records 3,000 photographs per hour, and 40,000 such photographs have been secured. It is shown that in no case does an oblique impact effect a disintegration. The argon nucleus remains intact even under the sharp impact of a helium nucleus from thorium-C'. J. F. S.

The Values of the Electrical Moments of the Atoms and their Connexion with other Quantities. R. D. KLEEMAN (*J. Franklin Inst.*, 1923, **196**, 479—493).—Assuming that atoms and molecules in their interactions are characterised by possessing definite electrical moments, which at 0° (absolute) are approximately independent of the density of the substance, the author shows from a consideration of the values of the internal heat of vaporisation of various substances that the electrical moments of atoms and molecules are, respectively, equal to $10^{-19}N^{2/3}$ and $10^{-19}\Sigma N^{2/3}$, in which N denotes the atomic number of the atoms concerned. The distance of separation of the electrical charges in the representative atomic doublet is shown to be equal to $2{\cdot}09\times10^{-10}N^{-1/3}$ cm., which is much smaller than the diameter of the atom. It is suggested that, in the case of the hydrogen atom, the nucleus is situated at a point distant $2{\cdot}09\times10^{-10}$ cm. from the centre of the circular path of the rotating electron and in a plane at right angles to the plane of motion. The doublet effect in the case of the more complicated atomic structures is probably attributable to the nuclei not occupying the foci of the electronic paths. It is shown that in the case of a number of substances, the respective values of the internal specific heat, c_i, at 0°, are related to the atomic weights a_w of the atoms constituting the molecules, by the equations $\log c_i=h_1\Sigma N^{2/3}=h_2\Sigma a_w{}^{1/2}$, where h_1 and h_2 are constants. More generally, at corresponding temperatures T, the relation takes the form $\log c_i=\phi(T/T_c)\Sigma N^{2/3}$, where T_c denotes the absolute critical temperature and $\phi(T/T_c)$ denotes a function of T/T_c. The application of the doublet effect to the subject of specific inductive capacity is briefly discussed.

J. S. G. T.

Formation of Gaseous Ions in the Oxidation of Nitric Oxide. A. K. BREWER and FARRINGTON DANIELS (*Trans. Amer. Electrochem. Soc.* [advance copy], 1923, 171—182).—Experiments with a special form of chamber show that when nitric oxide is oxidised between oppositely charged electrodes a current of electricity passes through the gases. The current is of the order of 10^{-14} amperes for the oxidation of 50 c.c. of nitric oxide per minute reacting in a field of 450 volts per cm. This corresponds with about one ion for every million molecules reacting. The current is directly proportional to the voltage and to the number of molecules reacting. No evidence of a saturation current could be detected. Various hypotheses to explain the results are advanced.

J. F. S.

Motion of Electrons in Helium. J. S. TOWNSEND and V. A. BAILEY (*Phil. Mag.*, 1923, [vi], **46**, 657—664).—In continuation

of previous work (A., 1922, ii, 43, 277, 494, 836), the authors have determined the velocities of translation and of agitation of electrons in helium submitted to the action of a uniform electric force, at various pressures ranging from 5 to 240 mm. of mercury. Values are deduced for the mean free path of the electron at 1 mm. pressure, and the proportion of energy lost by an electron on collision. The results indicate that, so calculated, the free path of an electron in helium is about twice that in hydrogen. The mean free path is approximately constant and equal to about 0·05 cm. for velocities between 10^8 and 5×10^7 cm. per sec. Moreover, the increase in the free path as the velocity diminishes occurs for smaller velocities in helium than in argon. The proportion of energy lost by an electron due to collision is approximately constant and equal to $2{\cdot}5 \times 10^{-4}$ for velocities ranging between 2×10^7 and 10^8 cm. per sec. For velocities greater than 10^8 cm. per sec., the proportion increases considerably owing to ionisation produced by the collision.

J. S. G. T.

The Motion of Electrons in Carbon Monoxide, Nitrous Oxide, and Nitric Oxide. M. F. SKINKER and J. V. WHITE (*Phil. Mag.*, 1923, [vi], **46**, 630—637).—In continuation of previous work, the authors have investigated the velocities of translation and of agitation of the electrons under various electrical forces and at various pressures, in the cases of the gases carbon monoxide, nitrous oxide, and nitric oxide. The results indicate that in the case of carbon monoxide the electrons in the stream do not tend to form ions by adhering to molecules of the gas, whilst such ions are produced in nitrous oxide and nitric oxide. Values of the mean free path of the electrons, the effective radius of the molecules, and the proportion of energy lost in collision between an electron and a molecule are tabulated. J. S. G. T.

Problems of Hydrone and Water: the Origin of Electricity in Thunderstorms. HENRY E. ARMSTRONG (*Nature*, 1923, **112**, 537—538).—If it is assumed that changes in the size of particles of water can, in the absence of conducting electrodes, give rise to free electricity, it is held that the coalescence of small drops is more likely to induce electrical phenomena than is the reverse process, in that energy is thereby liberated (cf. this vol., ii, 542). Chemical interchanges are believed to account for observations recorded by Simpson (*Phil. Trans.*, 1909, [*A*], **209**, 379) and Lenard (*Ann. Phys. Chem.*, 1892, [ii], **46**, 584). A. A. E.

Electrical Conductivity of Dilute Aqueous Solutions of Hydrogen Chloride. HENRY C. PARKER (*J. Amer. Chem. Soc.*, 1923, **45**, 2017—2033).—The electrical conductivity of aqueous solutions of hydrochloric acid has been determined at 25° for concentrations between 0·04 and 3·0 millimols. per litre. The solutions were made up by weight and were accurate to a few hundredths %, and the water had a specific conductivity of $0{\cdot}1 \times 10^{-6}$. The values for the equivalent conductivity show a slight maximum in the region of 0·1 millimol. per litre, due to the influence

of the impurities in the water, which apparently cause a somewhat greater effect than in the case of iodic acid (this vol., ii, 7). Comparison with the results of other investigators confirms the conclusions of Kraus and Parker (*loc. cit.*) regarding the considerable influence of the impurities in the water and of the alkali in glass cells on the electrical conductivity of dilute solutions of acids. Values have been interpolated for rounded concentrations from the results for hydrochloric and iodic acid. The data for iodic acid cover the range $0{\cdot}05 \times 10^{-3}N$ to $0{\cdot}5N$. The cell constant was determined by an intercomparison with three standard cells, over a considerable range of concentrations, with potassium chloride as electrolyte. The unusual results of this intercomparison may be explained by assuming the presence of an adsorbed layer in contact with the electrodes, the resistance of which is greater or less than that of the bulk of the solution, according to whether the electrolyte is negatively or positively adsorbed. One of the intercompared cells apparently has a greater correction for this adsorbed layer than the cell used in the measurements with hydrochloric acid, whilst the other two have a smaller correction. On the supposition that hydrochloric acid will be positively adsorbed and will consequently have but slight correction for this effect, a value for the constant was selected at the minimum point of the cell constant curve, which value is assumed to remain fixed in the measurements of the acid solutions. Extrapolation of the results on the assumption that the law of mass action is approached as a limiting form at infinite dilution gives a value of Λ_0 for hydrochloric acid of 425·69. Assuming that the value of Λ_0 for the chloride-ion at 25° is 75·8, a value of 349·89 is obtained for the hydrogen-ion at that temperature. Comparison of this with the value 349·93 obtained by Kraus and Parker (*loc. cit.*) for iodic acid leads to the value $349{\cdot}89 \pm 0{\cdot}05$ as the most probable value for the hydrogen-ion at 25°, since the basis for the cell constant is more firmly established for the measurements with hydrochloric acid. The mass-action constant corresponding with this extrapolation has a value 0·105.

J. F. S.

Electrical Conductivity Measurements on Dilute Aqueous Salt Solutions at 0°, 18°, and 100°. P. WALDEN and HERM. ULICH (*Z. physikal. Chem.*, 1923, **106**, 49—92).—Very exact electrical conductivity determinations have been made at 0°, 18°, and 100° with solutions of potassium chloride, nitrate, and perchlorate, sodium chloride and nitrate, cæsium nitrate, lithium perchlorate and picrate, tetraethylammonium picrate, potassium picrate, chlorate, bromate, and iodate in concentrations down to the most dilute. The limiting conductivity has been deduced by means of P. Hertz's hypothesis, and values have been found which confirm the hypothesis. Electro-conductivity–concentration curves have been drawn, and in the case of the less soluble salts it is found that regular deviations from the Hertz curve occur. Lithium picrate and tetraethylammonium picrate follow Stokes's law with sufficient exactitude in the temperature range examined. This result makes

it possible to determine the ionic mobility at 100° with satisfactory accuracy. In the case of the perchlorate-ion, ClO_4', the mobility at 18° equals 58·4, a value which is lower than the older measurements indicated. J. F. S.

Simple Determination of the Limiting Value of the Molecular Conductivity of Strong Electrolytes. C. DRUCKER (*Z. physikal. Chem.*, 1923, **105**, 472—475).—A criticism of Lorenz and Landé's papers (this vol., ii, 9, 284), in which it is shown that the statement that α is a constant characteristic of the substance is at variance with facts; the author shows that α expresses in its variability the accepted variability of the transport number. Consequently the suggested new extrapolation process is not applicable. J. F. S.

The Theory of Electrolytes. II. P. DEBYE and E. HÜCKEL (*Physikal. Z.*, 1923, **24**, 305—325).—In continuation of previous work (this vol., ii, 459), the authors present a mathematical analysis of the effect on the electrical conductivity of a completely ionised solution due to the presence of, and the mutual electric forces between, the ions. Ionic and electrophoretic forces are investigated, attention being directed to the following, among other matters: potential distribution around the moving ions, the motion of the solvent, and velocity and pressure distribution in the neighbourhood of the ions. An expression for the conductivity coefficient, f_λ, is derived in the form $1-f_\lambda=(4\pi\epsilon^2\nu n/DkT)^{1/2}[\epsilon^2 w_1/6DkT+bw_2]$, in which ϵ is the electronic charge, ν the total number of ions, n the number of molecules dissolved per c.c., D the dielectric constant of the solvent, k, Boltzmann's constant, T the temperature, w_1 and w_2 are complex valency factors, expressions for which are given, and b the mean diameter of the ions. This expression agrees with the conclusion of Kohlrausch (A., 1907, ii, 600), that in the case of dilute solutions, $1-f_\lambda \propto c^{1/2}$, c denoting the concentration. Results deduced from the expression are compared with experimental results in the cases of aqueous solutions of univalent and multivalent salts, and of non-aqueous solutions. Generally, the agreement between calculated and experimental results is satisfactory. J. S. G. T.

Relative Measurement of the Electrical Resistance of Thallium in the Region of the Temperature of Liquid Helium. H. KAMERLINGH ONNES and W. TUYN (*Arch. Néerland*, 1923, [iii], **6**, 284—292).—The electrical resistance of thallium has been determined at the temperature of liquid air, liquid hydrogen, and liquid helium with the object of ascertaining whether thallium is a super-conductor like mercury and lead. It is found that at 2·32°*K* all resistance has disappeared. J. F. S.

Relative Measurements of the Electrical Resistance of Ordinary Lead and Lead from Uranium at Temperatures below 14° *K*. H. KAMERLINGH ONNES and W. TUYN (*Arch. Néerland*, 1923, [iii], **6**, 293—300).—The electrical resistance of ordinary lead and lead from uranium (radium-*G*) has been deter-

mined and the point at which the resistance disappears ascertained. It has been found that pure lead (at. wt. 207·20) and uranium lead (at. wt. 206·06) have the same point of disappearance of resistance within 0·025°. J. F. S.

Electrical Resistance of Phenol–Water Systems, and the Application of [the Properties of] such Systems to Biological [Processes]. MARTIN H. FISCHER (*Kolloid Z.*, 1923, **23**, 131—147).—After a discussion of the theory of the colloidal condition, in which the lyophilic colloidal condition is defined as the product of two mutually soluble substances and is compared with the system phenol–water, the author describes a number of measurements of the electrical resistance of the system phenol-water to which various additions of acids, bases, salts, and non-electrolytes have been made. In these systems, the phenol phase is regarded as comparable with protoplasm, and the physico-chemical properties of this phase are regarded as of importance in the elucidation of the characteristic properties of living substance. Pure hydrated phenol has a very high electrical resistance, which is reduced by the addition of acids and alkalis. The addition of neutral salts also reduces the resistance, but not to so marked an extent. In all these cases, the amount of reduction is dependent, not only on the concentration of the added substance, but also on its chemical nature. The reduction caused by the addition of salts of constant concentration is not the same in all cases, and it is deduced that an "antagonism" exists in certain cases. Some non-electrolytes, such as the lower alcohols, also lower the resistance, but not so strongly as the electrolytes. The behaviour of hydrated phenol is parallel with that of cells and animal fluids under the same conditions. The presence of various electrolytes and non-electrolytes in mixtures of phenol and water changes the volume of the hydrated phenol phase. Acids slightly reduce the volume, whilst alkalis increase it considerably, that is, they bring about a swelling of the phenol. Salts reduce the volume in proportion to their concentration. This behaviour is parallel with the absorption and loss of water in living cells, which is usually attributed to changes in osmotic pressure. Protoplasm is not, as is so generally held, a solution of protoplasmic materials in water, like phenol in water, but a system of the opposite type, namely, water dissolved in protoplasmic material, like water in phenol. The physico-chemical laws which apply to the latter type of system alone hold for living material. J. F. S.

Single Potential of Arsenic and its Power to Replace other Metals in Solutions. LOUIS KAHLENBERG and JOHN VERNON STEINLE (*Trans. Amer. Electrochem. Soc.* [advance copy], 1923, 203—226).—The single potential of arsenic has been determined in a number of different electrolytes, including arsenic trichloride, tri-iodide, arsenious oxide, *p*-aminophenylarsinic acid, *p*-hydroxyphenylarsinic acid, *p*-glycinoaminophenylarsinic acid, *p*-acetamidophenylarsinic acid, and di-*p*-aminophenylarsinic acid, and in general the results of previous investigators have been confirmed. In making

the single potential measurements, the arsenic electrodes were prepared in a number of different ways. It was found that a solid arsenic electrode, sawn from a large piece of arsenic, gives trustworthy results, and offers on the whole the best form of electrode for making the determinations. Electrodes prepared by electroplating arsenic on other metals were found to yield untrustworthy results, in that they do not develop the true potential of pure arsenic. Metallic arsenic was used to displace the metals silver, copper, and mercury from their compounds. The reaction which occurs in these cases may be represented by $6MX+2As+3H_2O=6M+6HX+As_2O_3$. Arsenic has been displaced from its compounds by other metals, including sodium, magnesium, aluminium, zinc, cadmium, iron, cobalt, nickel, lead, tin, bismuth, and antimony. In many of these cases the replacement could not have been predicted from a knowledge of the single potentials of the metals concerned. The authors are of the opinion that in the case of arsenic the power of a metal to replace this metal is a highly specific property which depends on the individual nature of the metals in question and also on the liquids used in the experiments.

J. F. S.

Electric Potential of Antimony–Lead Alloys. S. D. MUZAFFAR (*Trans. Faraday Soc.*, 1923, **19**, 56—58).—Measurements of the electric potential of antimony–lead alloys against a calomel electrode in *N*-potassium hydroxide, *N*-lead nitrate, and acid potassium antimony tartrate solutions showed that up to 98% of antimony the potentials were identical with that of lead, thus demonstrating that, in the antimony-lead series, there are no solid solutions and no compounds formed. A. R. P.

Oxidation–Reduction. III. Electrode Potentials of Mixtures of Indophenol-1-Naphthol-2-Sulphonic Acid and the Reduction Product. W. MANSFIELD CLARK and BARNETT COHEN (*U.S. Pub. Health Rep.*, 1923, No. 834, 3—28; cf. this vol., ii, 677).—A new indophenol, 4-*indophenol*-1-*naphthol*-2-*sulphonic acid*, $HO\cdot C_6H_4\cdot N:C_{10}H_5(SO_3H):O$ or $O:C_6H_4:N\cdot C_{10}H_5(OH)\cdot SO_3H$, has been synthesised by grinding 14·2 g. of quinone chloroimide with 25 g. of water and a quantity of ice, then with continual grinding adding 24·6 g. of sodium 1-naphthol-2-sulphonate in 75 c.c. of 4*N*-sodium hydroxide. The solution is kept for an hour. A cold saturated salt solution is then added, when a thick precipitate is formed. This is filtered and washed with cold saturated salt solution. The material is extracted with water and filtered. The filtrate is cooled and precipitated with carbon dioxide. The precipitate, after drying on porous plates, is recrystallised from alcohol, when a red sodium salt of the above-named compound separates. The reduction potentials of this compound in equilibrium with its reduction product at different P_H values have been determined at 30°. It is found that the measurements conform fairly with the equation $E_h=0{\cdot}5440-0{\cdot}03006\log[S_r]/[S_0]+0{\cdot}03006\log(K_rK_2[H^{\cdot}]+K_r[H^{\cdot}]^2\ldots+[H^{\cdot}]^3)-0{\cdot}03006\log(K_0+[H^{\cdot}])$, where S_r is the concentration

of the total reductant, $[S_0]$ that of the total oxidant, K_r the dissociation constant of that phenolic group in the reductant which is possessed by the oxidant, K_0 is the dissociation constant of the same group in the oxidant, and K_2 is the dissociation constant of the phenolic group created by the reduction. The following values are obtained: $K_0=2{\cdot}09\times10^{-9}$, K_r $8{\cdot}01\times10^{-10}$, and $K_2=2{\cdot}00\times10^{-11}$. The hypothetical normal potential is $+0{\cdot}5440$ volt. It is shown that an 80—90% reduction of 4-indophenol-1-naphthol-2-sulphonic acid within the ordinary physiological range of P_H indicates a reduction potential about 0·52 volt more positive than the hypothetical hydrogen electrode potential of the solution, and it is suggested that the reduction of this dye should indicate minute degrees of physiological reduction. J. F. S.

Reduction Potentials of Quinones. I. The Effect of the Solvent on the Potentials of certain Benzoquinones. James B. Conant and Louis F. Fieser (*J. Amer. Chem. Soc.*, 1923, **45**, 2194—2218; cf. A., 1922, ii, 547; this vol., ii, 9, 285).—The reduction potentials of various alkyl and chloro-derivatives of benzoquinone have been measured in alcoholic and in aqueous solution. A method has been devised whereby the free energy of reduction of a quinone, and the reduction potential, referred to the solid state, can be found. A cell is constructed consisting of a hydrogen electrode, immersed in a given solvent, connected with a half-cell containing an inert electrode immersed in the same solvent saturated with both the quinol and the quinone, and containing both solid substances. From the potential of this combination it is possible to calculate directly the free energy of reduction, referred to the solid states. This method cannot be used, however, if a quinhydrone is formed; the following procedure is then adopted. Two separate combinations are investigated. In one the half-cell contains a solution saturated with the quinone and the quinhydrone; in the other, the solution is saturated with the quinol and the quinhydrone. The algebraic mean of the potentials of the two combinations is the required reduction potential referred to the solid states, whilst the difference between the potentials is a measure of the free energy of the formation of the solid quinhydrone from its solid components. The results obtained show that, either in solution or referred to the solid states, the introduction of methyl groups into the quinone nucleus decreases the reduction potential, whilst the introduction of chlorine atoms at first raises the potential and then lowers it. Essentially the same relationships are found between the reduction potentials of different substances in aqueous and alcoholic solution, but the potentials referred to the solid states are not entirely parallel to those measured in solution. The temperature coefficient of the reduction potential (solid states) has been measured for all the quinones investigated, and the total energy of reduction calculated. Comparison with previous thermochemical measurements reveals, probably owing to errors inherent in the latter, great discrepancies in the figures for the polychloroquinones. W. S. N.

Membrane Potentials Considered as Diffusion Potentials. E. B. R. PRIDEAUX and W. E. CROOKS (*Chemistry and Industry*, 1923, **42**, 955).—Measurements of conductivities, viscosities, diffusion, and membrane potentials in solutions of potassium benzoate and potassium salicylate with parchment membranes, show a definitely diminished mobility of the organic anions in the parchment; this retardation accounts for the increase of the diffusion potential with such salts. C. R. H.

Behaviour of Cuprous Oxide Photo-voltaic Cells. ALLEN D. GARRISON (*J. Physical Chem.*, 1923, **27**, 601—622).—The formation of cuprous oxide electrodes and the conditions under which they have both a positive and a negative light effect are described and the general characteristics of each effect discussed. The positive photo-potential is found to be approximately proportional to the logarithm of the light intensity and to increase with increasing hydrogen-ion concentration. The maximum negative photo-potential is proportional to the intensity of the light for low intensities and constant at high intensities, whilst the positive recoil following the negative maximum increases with the intensity. The maximum negative photo-potential decreases with increasing hydrogen-ion concentration. For large effects, the negative photo-potential decreases and for small effects increases with increasing cupric-ion concentration. The characteristics of the cuprous oxide electrodes which are now known are all explained by the established laws of electro-chemistry by the assumption that the light displaces the equilibrium constant of the reaction, Cu_2O (solid) $\leftrightarrow$ Cu_2O (dissolved) $\leftrightarrow 2Cu^{\cdot}+O''$, causing the cuprous oxide to behave as though its solubility was increased in the light. The results are what would be expected if Einstein's photo-chemical law applied to this reaction in a qualitative manner. The active frequencies have not yet been determined. The theory is also applicable to the silver halide electrodes as well as to the copper electrodes, since they behave in the same way, and is opposed to the theory that the primary effect of radiation is either photoelectric in its nature or causes a direct separation of the uncharged elements. The hypothesis that the effect of the light is a separation of the charged elements as ions or thereby an increase in the solubility of the salt and that the decomposition is made complete only by electrochemical equilibrium is supported by the experimental fact that perfectly dry salts are stable in light. J. F. S.

The Electromotive Behaviour of Magnesium. II. A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **26**, 395—407; cf. A., 1921, ii, 402).—The effect of amalgamation on the *E.M.F.* of the magnesium electrode was studied. From theoretical considerations it was found that the magnesium electrode cannot possibly behave as an oxygen or hydrogen electrode, but that the explanation of its low *E.M.F.* is to be found in the fact that the formation of a layer of hydroxide on the surface of the metal hinders the establishment of the metal–hydrogen inner equilibrium. Activation by means of mercury causes the true inner equilibrium

to be approached more closely. By actual measurement it was found that the potential of a magnesium half-element containing $M/10$-magnesium sulphate was $-1{\cdot}902$ volt with respect to a normal calomel electrode, but that on the addition of 3% of a saturated solution of mercuric chloride it fell to $-1{\cdot}740$ volt. On removing the magnesium, washing with distilled water, and immersing in $M/10$-pure magnesium sulphate, it showed immediately an *E.M.F.* of $-1{\cdot}898$ volt, and, after five minutes, one of $-1{\cdot}956$ volt.

H. H.

Electrolysis with an Aluminium Anode the Anolyte being: I. Solutions of Sodium Nitrite. II. Solutions of Potassium Oxalate. F. H. JEFFREY (*Trans. Faraday Soc.*, 1923, **19**, 52—55).—Electrolysis of solutions of sodium nitrite in concentrations varying from normal to saturated resulted in the formation of much aluminium hydroxide and in the evolution of nitric oxide, whilst nitric acid was found in the anolyte. Probably the primary product at the anode is aluminium nitrite, which is immediately hydrolysed to aluminium hydroxide and nitrous acid. The latter compound then decomposes into nitric oxide and nitric acid.

Electrolysis with potassium oxalate solution as the anolyte resulted in the aluminium anode dissolving; on evaporation of the liquid, well-developed, colourless crystals of potassium alumini-oxalate, $K_3Al(C_2O_4)_3,3H_2O$, were obtained analogous to potassium chromi-oxalate.

A. R. P.

The Electron in the Chemistry of Solutions and in Electrochemistry. I. The Paths of Electrons in Solutions during Electrolysis with a Spark Cathode. L. V. PISARSHEVSKI and (MLLE) M. ROSENBERG (*J. Russ. Phys. Chem. Soc.*, 1923, **54**, 533—547).—A solution of $N/4$-potassium iodide was electrolysed, keeping the cathode 3—4 cm. above the surface of the liquid so that a spark was produced. The addition of phenolphthalein causes the appearance of a red stream in the liquid along the path of the spark through the liquid; a blue stream is observed under the same conditions if starch be added instead of the phenolphthalein, whilst the colour of the stream is violet if both indicators are added together. Under the standard conditions adopted, the stream was usually visible to a depth of about 9 cm., and widened at the end, and it was observed that the red streams were somewhat more tortuous and irregular than the blue ones. The streams are deflected by the introduction of a magnetic field, and are due to a pencil of electrons, unaccompanied by matter, being projected into the liquid from the cathode. These electrons encounter ions of iodine and cause them to lose their electrons or become oxidised, the atomic iodine then reacting with the starch in the usual way. A secondary process is the reduction of potassium-ions, which acquire an additional electron and become atomic potassium; this then reacts with water, producing potassium hydroxide, which ionises and is detected by the red coloration of the phenolphthalein. It appears likely that the reduction of the potassium-ions is due both to the electrons lost by the iodine-ions and those of the cathode stream. These experiments

are thus a demonstration of the fact that the process of oxidation is the loss of an electron, whilst reduction involves the acquisition of an electron by an ion. G. A. R. K.

The Electron in the Chemistry of Solutions and in Electrochemistry. II. The Electrons of Radium as a Reducing Agent and α-Particles as an Oxidising Agent. L. V. PISARSHEVSKI (*J. Russ. Phys. Chem. Soc.*, 1923, **54**, 548—570).—Aqueous solutions of hydrogen iodide (0·5*N*) and ferrous chloride were kept in contact with a radium preparation for about a year; the radium preparation was introduced directly into the solution in some cases and in others was contained in a separate glass vessel sufficiently thick to absorb all α-particles; control solutions were also kept. It was found that oxidation took place to an appreciable extent in solutions containing the radium preparation, iodine being liberated and ferrous-ions being converted into ferric-ions. No decomposition of the solvent was observed, doubtless because the oxygen and hydrogen produced were immediately acted on by the dissolved substances. It is shown by calculation that the results obtained can only be explained on the assumption that the ions of ferrous iron and iodine are oxidised, that is, they lose a valency electron, when they collide with α-particles derived from the radium salt. It was found that hydrogen iodide exposed to bombardment by β-particles (or electrons) alone showed slight but definite signs of decomposition; the action is explained by the absorption of the electrons by the ions of iodine. In solutions containing radium, this reducing process goes on concurrently with the oxidation due to α-particles, but the latter process predominates owing to the fact that α-particles are given out in far greater number than β-particles. In connexion with these experiments, the nature of chemical and electrochemical processes is discussed. G. A. R. K.

The Electron in the Chemistry of Solutions and in Electrochemistry. III. The Electronic Nature of Ionic Reactions and their Capacity to Produce a Current. L. V. PISARSHEVSKI and (MLLE) M. ROSENBERG (*J. Russ. Phys. Chem. Soc.*, 1923, **54**, 570—600).—When two unequal platinum plates are dipped in a solution in which a chemical reaction is proceeding and the plates are connected together through a sensitive galvanometer, the passage of a current is observed. The current is due to the following causes. Every ionic reaction, such, for instance, as oxidation or reduction (cf. preceding abstract), involves the passage of electrons to and fro in the reacting medium. Some of these encounter the platinum plates dipping in the liquid and communicate an electric charge to them by virtue of a two-fold process; some electrons will encounter atoms of platinum with force sufficient to remove valency electrons from them, that is, causing the ionisation of the metal, whilst other electrons will merely enter the plates, increasing the concentration of electrons within it (the two processes are evidently mutually opposed). If it now be assumed that the electronic concentration in the two plates is not the same, it is clear that a current must be produced when they are joined by a wire; it is proved that if

the plates are of unequal dimensions, such is actually the case, and if the potential is due to the electrons acquired from the solution the larger plate is negatively charged whilst the smaller one is positive. The converse is, however, the case, if the chief process depends on the loss of electrons by the plates, favoured by the presence in the solution of some reagent ready to unite with the electrons set free. The larger plate then becomes positive and the current flows from the smaller plate to the larger; this is particularly noticeable in reactions involving oxidation and reduction, in accordance with the authors' view of these processes (preceding abstracts). Processes of ionic dissociation also produce an appreciable current under these conditions, and it is significant that the current is increased if pure water be added to the solution so as to cause increased ionisation of the electrolyte. The direction of this current is, however, dependent on the existence and relative magnitude of two processes, the ionisation of the electrode when brought into contact with the solution and the dissociation of the solute with a consequent movement of electrons; these two processes cause changes in opposite directions, and therefore the current between two unequal platinum plates dipped in a salt solution may pass in either direction, according to circumstances.

The influence of a radioactive substance on the phenomenon is described, and the observations of Schtschukarev (A., 1916, ii, 172) bearing on some aspects of the subject are discussed. G. A. R. K.

Electro-endosmosis and Electrolytic Water Transport. HEINRICH REMY (*Z. Elektrochem.*, 1923, **29**, 365—370).—The author has determined the electrolytic transport of water as well as the water transported by electro-endosmosis for a number of normal and decinormal solutions. The water carried electrolytically is that which forms a layer round the ions, and in consequence is carried along with them. The amount of water carried in this way furnishes a measure of the number of molecules of water associated with each ion. The results show that the amount of water associated with the alkali-ions including ammonium follows the same order as has been previously calculated by the author from a comparison of the mobilities of these ions (A., 1915, ii, 310). The positive electrolytic water transport of the acids examined shows that the hydrogen-ions are sheathed in a small amount of water. The amount of water connected in this way lies between one and two molecules for each hydrogen-ion on the assumption that the water sheath of the chlorine-ion contains between three and nine molecules. J. F. S.

Velocity of Migration of Isomeric Ions. I. H. LEY and H. DIEKMANN (*Z. physikal. Chem.*, 1923, **106**, 161—177).—The authors have redetermined the electrical conductivity of the sodium or potassium salts of *o*-hydroxybenzoic acid, *p*-hydroxybenzoic acid, *p*-cresotic acid, 6-hydroxy-*m*-toluic acid, *o*-hydroxybenzene-sulphonic acid, *p*-hydroxybenzene sulphonic acid, anisic acid, and *o*-methoxybenzoic acid at 25° for a number of dilutions, and the molecular conductivity at infinite dilution has been obtained in each case. From these values, on the basis of $\lambda_{Na^{\cdot}}=50{\cdot}2$, the ionic

mobility of the anions has been deduced and the following values obtained: $OH \cdot C_6H_4 \cdot CO_2'$ [*o*] $\lambda_a=36 \cdot 8$; [*p*] $\lambda_a=31 \cdot 5$. $OH \cdot C_6H_3Me \cdot CO_2'$, [$Me:OH:CO_2'=1:3:4$] $\lambda_a=34 \cdot 4$; [$Me:OH:CO_2'=1:2:3$] $\lambda_a=34 \cdot 4$; [$Me:OH:CO_2'=1:3:6$] $\lambda_a=30 \cdot 5$. $OMe \cdot C_6H_4 \cdot CO_2'$ [*o*] $\lambda_a=33 \cdot 5$; [*p*] $\lambda_a=33 \cdot 3$; $OH \cdot C_6H_4 \cdot SO_3'$ [*o*] $\lambda_a=35 \cdot 5$; [*p*] $\lambda_a=33 \cdot 9$. The results are discussed in connexion with the orientation of the compounds. J. F. S.

The Constitution of Soap Solutions: Migration Data for Potassium Oleate and Potassium Laurate. James William McBain and Richard Charles Bowden (T., 1923, **123**, 2417—2430).

Crystalline Form of Electro-deposited Metals. William Blum and H. S. Rawdon (*Trans. Amer. Electrochem. Soc.* [advance copy], 1923, 245—267).—A simple hypothesis of the mechanism of crystal formation in electro-deposition is put forward, according to which the cathode discharge of metal-ions and the formation of crystals constitute one and the same process, and any given ion is discharged at the point at which the lowest discharge potential is required. The discharge potential is a function of the solution pressure of the metal and the "effective" metal-ion concentration adjacent to it. The single potential and solution pressure of a metal are the resultant of the "primary single potential," which is defined in terms of the solution pressure of a single unorientated atom, and the "orientation potential," which is a measure of the diminution in solution pressure and corresponding algebraic increase in single potential caused by the arrangement or orientation of the adjacent metal atoms. A higher potential is required to discharge an ion in a position unrelated to those of previously discharged atoms than on an existing crystal, and similarly a higher potential is required to discharge an ion on a small crystal than on a large one. Typical structures of electrode deposits are classified into three major groups: those in which all, or practically all, of the initial nuclei continue to grow, those in which only a part of the initial nuclei continue to grow, and those in which none of the initial nuclei grow. The factors which determine the character of the crystals are discussed and the direction of the change produced by any change in operating conditions is predicted and illustrated. J. F. S.

Passivity. Gerhard C. Schmidt (*Z. physikal. Chem.*, 1923, **106**, 105—154).—Attempts to measure the solubility of hydrogen and oxygen in iron, platinum, chromium, nickel, gold, and copper have been made by liberating these gases electrolytically on one side of a metal electrode and measuring the potential of the other side against a normal calomel electrode. The effect of leading hydrogen and oxygen over surfaces of copper, iron, nickel, chromium, platinum, and gold on the potential of these metals in various solutions has also been determined. The effect of roughening and polishing the surface of chromium, iron, molybdenum, nickel, tantalum, vanadium, and platinum on the potential of these metals has been determined. The results of the above determinations are

discussed in connexion with the passivity phenomena of the metals. It is shown that Warburg's hypothesis (*Ann. Phys. Chim.*, 1889, [iii], **38**, 321) that the change of potential brought about by the passage of hydrogen or oxygen over a metal is due to changes of concentration in the surrounding solution is not confirmed by the present experiments. On the other hand, the hypothesis which states that gases dissolved in metals change the potential on account of their solution pressure is found to be in agreement with the experiments. No sure conclusions with respect to activity or passivity can be drawn from potential measurements alone, since the potential depends for the most part on whether the gas is dissolved or not in the metal. Chromium, nickel-chromium-steel, molybdenum, and tantalum after polishing give a very low potential which reaches the normal value again in fifty minutes with chromium, thirty minutes with molybdenum, and twenty minutes with tantalum. In the case of nickel, cobalt, and vanadium the change of potential is nothing like so great as in the above cases and it regains its normal value much more rapidly. Platinum, copper, antimony, aluminium, and iron exhibit a still smaller change of potential on polishing and in the case of zinc, tellurium, magnesium, cadmium, tin, and lead the change of potential is so small as to be scarcely detectable. The presence of gases or polarisation take no part in these changes. A complete parallelism exists between the amount of the change of potential, the time required for the metal to regain its normal potential, and the hardness of the metal. Thus the hardest metal, chromium, exhibits the largest change in potential and requires the longest time to regain its normal potential. This phenomenon is attributed to the diminution of the surface tension. Passive nickel becomes active when its surface is chemically attacked; this can occur by means of electrolytes such as sulphuric acid or by chlorine, bromine, or iodine. On account of the passivity of nickel, iodine separates at first in the electrolysis of potassium iodide solutions, but when the surface of the nickel has been attacked, nickel iodide is formed and the metal is then active. Nickel can also be activated by the removal of gases from its surface and by mechanically roughening the surface. Passive chromium becomes active by disturbing the surface, by scratching, knocking, and so on, but in nitric acid it remains permanently passive. Activated chromium placed in dilute hydrochloric or sulphuric acid remains permanently active. On removal from the acid, however, it becomes passive again after a short time, even although oxygen is rigorously kept away. Chromium heated in a vacuum or in nitrogen is active. In hydrochloric acid at 100° it is also active, and at this temperature chlorine, bromine, and iodine attack chromium and activate it, solely because the surface is disturbed. When hydrogen is evolved from one side of a sheet of iron the other side becomes active; diffusing oxygen acts in the same way. Even in a solvent in which iron does not dissolve, for example, a solution of potassium nitrate, it may be activated as above. This fact is in direct opposition to the oxidation and oxygen-alloy hypotheses. In addition to its activating action, oxygen also shows a passivating action. Iron becomes

passive in a solution of chromic acid which contains a trace of sulphuric or hydrochloric acid; it may be activated by diffusing hydrogen or by disturbing the surface. The passivity of metals is therefore to be attributed to a large surface tension, for when the surface tension is reduced the metal becomes active. Reduction of the surface tension can be brought about by attacking the surface chemically, by disturbing the surface mechanically, or by causing gases to escape from the surface. Oxygen passivates and hydrogen activates. J. F. S.

Relation between Current, Voltage, and the Lengths of Carbon Arcs. II. A. E. R. WESTMAN and W. J. CLAPSON (*Trans. Amer. Electrochem. Soc.* [advance copy], 1923, 87—100).—Conditions have been found under which steady arcs can be maintained with currents from 120 to 700 amperes and voltages from 15 to 60. The appearance of steady arcs and of the various unsteady arcs that were encountered are described. A technique for accurately determining the relationship between current, voltage, and the length of carbon arcs has been developed, and has led to results which are tabulated in the paper. These results lead to the conclusion that $e=0{\cdot}99L$, where e is the voltage over the arc and L the length in millimetres from the tip of the cathode to the bottom of the anode crater. J. F. S.

Spectroscopic Magneton Numbers. A. SOMMERFELD (*Physikal. Z.*, 1923, **24**, 360—364).—The author considers the physical reality of the magneton, in accordance with the ideas of Gerlach (*Physikal. Z.*, 1923, **24**, 275) and of Epstein (*Science*, 1923, **57**), to be definitely established from a consideration of the series of multiplets in the spectra of chromium and manganese. It is shown that whereas in the transition from group to group in the periodic classification of the elements the value of the atomic magnetic moment associated with the atomic condition responsible for the emission of the lines of greatest multiplicity increases by one unit, the mechanical moment or the internal quantum number corresponding thereto increases by half a unit only. This result the author considers to be the basis of the explanation of certain apparent magneto-optic and magneto-mechanical anomalies, including the Richardson effect. J. S. G. T.

Determination of the Isothermals of Hydrogen and Helium at Low Temperatures, made with the Object of examining whether the Compressibility of these Gases is Influenced by the Quanta. J. PALACIOS MARTINEZ and H. KAMERLINGH ONNES (*Arch. Néerland*, 1923, [iii], **6**, 253—276).—With the object of ascertaining whether or no the compressibility of hydrogen and helium is influenced by the quanta, the authors have determined the isothermals of these two gases at 20·50°. The values of δ_A and pv_A have been calculated, and it is shown that the product pv_A is practically a linear function of the density δ_A. It is concluded from this fact that the quanta exert no influence on the form of the isothermals, a result which is contrary to the demands of the hypothesis advanced by Sackur and by Keesom. J. F. S.

Isothermals of Oxygen at 0° and 20°. H. A. KUYPERS and H. KAMERLINGH ONNES (*Arch. Néerland*, 1923, [iii], **6**, 277—283).—The isothermals of oxygen have been determined at 0° and 20°, and the values of pv_A, d_A, and p tabulated and compared with the calculated value of pv_A. The experimental values when plotted lead to a parabolic curve represented by the equation $pv_A = A_A + B_A d_A + C_A d_A^2$, for which the constants have been ascertained in the usual manner. These have the values for 0°, $A_A = 1{\cdot}000956$, $B_A = -0{\cdot}95803 \times 10^{-3}$, $C_A = 2{\cdot}0608 \times 10^{-6}$ and for 20°, $A_A = 1{\cdot}07426$, $B_A = -0{\cdot}80379 \times 10^{-3}$ and $C_A = 2{\cdot}0591 \times 10^{-6}$. By means of these coefficients the coefficient of dilation under constant pressure has been calculated and the following values have been obtained: $p=20$, $[\alpha_{t,p}]_0^{20} = 0{\cdot}00393$, $p=40$, $\alpha = 0{\cdot}00425$, and $p=60$, $\alpha = 0{\cdot}00449$.

J. F. S.

Influence of Small Variations of Temperature on the Conductivity of Solid Salts and the Rôle of Humidity in the Phenomenon. P. VAILLANT (*Compt. rend.*, 1923, **177**, 637—639).—The temperature-conductivity curves for heating and cooling are identical when the material examined has been previously powdered and dried. With compressed, ground material (sodium chloride), not previously dried, or with a crystalline layer of material (Iceland spar), the conductivity at first rises rapidly with increase of temperature, reaches a maximum and then decreases steadily, the decrease continuing on cooling. At the original temperature, the material shows a smaller conductivity than at the outset. A second heating gives similar results, but the conductivity variations are smaller, whilst a third heating is accompanied by no variations. The loss of conductivity is, however, temporary, for on leaving the material exposed for some hours, it not only regains its conductivity, but then possesses a greater conductivity, and the above temperature effects are more pronounced than before. The conductivity in these cases is apparently a surface effect; it is decreased or increased by exposure of the material to a dry or wet atmosphere respectively.

E. E. T.

Melting Point of Ice on the Absolute Scale. LEIGHTON B. SMITH and ROBERT S. TAYLOR (*J. Amer. Chem. Soc.*, 1923, **45**, 2124—2128).—The value, T_0, the absolute temperature of melting ice, from the nitrogen volume and pressure expansion coefficients gives a mean value of 273·12° (see this vol., ii, 755). The mean value obtained by using the data of other gases including the Joule-Thomson coefficient is 273·13±0·01°. J. F. S.

The Use of Rast's Camphor Method for Micro-determinations of the Molecular Weight of Liquids. J. HOUBEN (*J. pr. Chem.*, 1922, [ii], **105**, 27—30).—Rast (A., 1922, ii, 421) has determined the molecular weight of four solid substances, by measuring the depression in the freezing point of camphor, using small quantities of material, and determining the freezing point by the capillary tube method. It is now shown that this procedure may be adopted to determine the molecular weight of any liquid

of fairly high boiling point. Excellent agreement with the theoretical figures is obtained for *n*-heptyl alcohol, geraniol, terpineol, methyl salicylate, methyl anthranilate, aniline, *n*-decyl alcohol, benzyl benzoate, ethyl benzoate, methyl nonyl ketone, benzonitrile, and tetrachloroethane. W. S. N.

Azeotropic Mixtures. SYDNEY YOUNG (*Proc. Roy. Irish Acad.*, 1922, [*B*], 36, 22—30).—The question whether two or three given liquids are likely to form a binary or ternary azeotropic mixture, of minimum or maximum boiling point, is discussed. No ternary azeotropic mixture of maximum boiling point has yet been discovered. Values of the boiling points of members of the methyl alcohol series from methyl to *n*-octyl alcohol inclusive are tabulated. The following are the values of the boiling points of binary and ternary azeotropic mixtures of the respective alcohols with water (represented by the symbol *w*), hexane (symbol *h*) benzene (symbol *b*), and toluene (symbol *t*), so far as these have been determined: methyl: *h*, 50·0°; *b*, 58·35°; ethyl: *w*, 78·15°; *h*, 58·7°; *b*, 68·25°; *t*, 76·7°; *h*, *w*, 56·6°; *b*, *w*, 64·85°; *t*, *w*, 74·55°; *iso*propyl: *w*, 80·37°; *h*, 61·0°; *b*, 71·9°; *t*, 80·6°; *h*, *w*, 58·2°; *b*, *w*, 66·5°; *t*, *w*, 76·2°; *tert*.-butyl: *w*, 79·9°; *h*, 63·7°; *b*, 73·95°; *h*, *w*, 58·9°; *b*, *w*, 67·3°; *n*-propyl: *w*, 87·7°; *h*, 65·65°; *b*, 77·1°; *t*, 92·6°; *h*, *w*, 59·95°; *b*, *w*, 68·5°; *t*, *w*, 80·05°; *sec*.-butyl: *w*, 88·5°; *h*, 67·5°; *b*, 79°; *h*, *w*, 61·1°; *tert*.-amyl, $CMe_2Et·OH$: *w*, 87° (?); *h*, 68·5°; *t*, 99·2°; *t*, *w*, 82°; *iso*butyl: *w*, 89·9°; *h*, 68·1°; *b*, 79·85°; *t*, 101·15°; *t*, *w*, 83°; *n*-butyl: *w*, 92·25°; *t*, 105·5°; *iso*amyl, $CHMe_2·CH_2·CH_2·OH$: *w*, 95·15°; *t*, 110·5°; *n*-octyl: *w*, 98°. Methyl alcohol forms no azeotropic binary mixtures with water, benzene, or toluene, and no azeotropic ternary mixtures with the respective systems hexane–water, benzene–water, or toluene–water. *iso*Butyl alcohol forms no azeotropic ternary mixture with the system hexane–water. It is possible that the amyl alcohol, $CMe_3·CH_2·OH$, may form an azeotropic mixture with hexane, but much less probable that the amyl alcohol, $CHMe_2·CHMe·OH$, forms such a mixture. It may be regarded as certain that none of the alcohols with higher boiling points do so. No alcohol with a higher boiling point than 108° should form a ternary azeotropic mixture with hexane and water, nor form a binary mixture with benzene. It is uncertain whether *sec*.-butyl alcohol forms a ternary mixture with benzene and water; it is almost certain that *tert*.-amyl alcohol does not. Alcohols of higher boiling point cannot form ternary azeotropic mixtures with benzene and water. The existence of a binary methyl alcohol–toluene azeotropic mixture is doubtful. The b. p. of the amyl alcohol, $CMe_3·CH_2·OH$, is probably 112°. J. S. G. T.

Vapour Pressure Thermometer. ALFRED STOCK (*Z. Elektrochem.*, 1923, 29, 354—358).—A full description of the method of making and filling of a vapour pressure thermometer previously described by Henning and Stock (A., 1921, ii, 432). The original must be consulted for details and dimensions. The thermometer filled with carbon disulphide has a range from the ordinary temper-

ature to $-10°$, with sulphur dioxide $-10°$ to $-40°$, with ammonia $-30°$ to $-77°$, with carbon dioxide $-75°$ to $-100°$, hydrogen chloride $-85°$ to $-111°$, ethylene $-100°$ to $-150°$, methane $-150°$ to $-185°$, and with oxygen $-180°$ to $-200°$. A very complete table of vapour pressures from about 1,000 mm. downward with the corresponding temperatures is given for all the gases named above. The thermometer is capable of an accuracy sufficient for most purposes. J. F. S.

The Vapour Pressures of Concentrated Sucrose Solutions. EDGAR PHILIP PERMAN and HORACE LEONARD SAUNDERS (*Trans. Faraday Soc.*, 1923, **19**, 112—116).—The curves showing the relation between the vapour pressure of sucrose solutions and the concentration of the sugar at 70° and 90° have been determined and found to be smooth curves and not straight lines as previously found by Perman and Price (A., 1913, ii, 20). From these curves the value of the hydration factor a in Callendar's formula, $p'/p=(N-an)/(N-an+n)$, is found to be 5 between concentrations of 20 and 65 g. of sugar per 100 c.c. Babo's law holds for sugar solutions up to a concentration of 80% of sugar. A. R. P.

Improved Methods of Evaporation in the Laboratory. H. G. BECKER (*Sci. Proc. Roy. Dubl. Soc.*, 1923, **17**, 241—248).—Experiments were made to determine the rate of evaporation of distilled water at different temperatures in still air and in air currents of different speeds. Using an open dish in an oil-bath, a bath temperature of 100° gives a water temperature of 70° in still air and of 54° in a strong draught. To maintain the water at 100°, bath temperatures of 170° and 215° are needed in still air and a strong draught respectively. The rate of evaporation increases very rapidly at higher temperatures, and between 90° and 100° each degree rise is about six times as effective as between 30° and 40°. The air current is relatively more effective at lower temperatures, on account of its greater cooling effect at high temperatures. The normal rate of evaporation on a water-bath in still air is 0·01 c.c. per minute per sq. cm. This can be increased without difficulty to 0·07 c.c. per sq. cm. by raising the dish temperature to 95° and using an air draught of 500 feet per minute. An effective apparatus for evaporating solutions is described, consisting of a glass bulb blown in a wide-bore tube, mounted horizontally and rotated whilst heated with a gas burner. A current of air may be passed through the bulb, or it may be evacuated. In this apparatus superheating is entirely avoided, and such substances as ferric chloride may be readily crystallised. E. H. R.

Calorimetric Micro-bomb. M. PADOA and B. FORESTI (*Gazzetta*, 1923, **53**, 493—498).—Heats of combustion may be determined with a high degree of accuracy by means of a small bomb calorimeter inserted in an ice calorimeter of the Bunsen form. Only 0·03—0·06 g. of the substance is required, this being weighed on a microbalance. [Cf. *J.S.C.I.*, 1923, 1045A.] T. H. P.

The Heat of Combination of the Metals of the Alkaline Earths with Oxygen, Hydrogen, and Nitrogen. A. GUNTZ and F. BENOIT (*Ann. Chim.*, 1923, [ix], **20**, 5—33; cf. this vol., ii, 126).—The following heats of formation were determined: Strontium hydride, 42·2 cal.; barium hydride, 40·9; strontium nitride, 31·8; barium nitride, 31·3; calcium amide, 93·0; lithium amide, 86·7 (for $2LiNH_2$); strontium amide, 84·3; barium amide, 80·24; lithium imide, 52·6; barium imide, 54·4. In each case the measurement depended on the heat developed when the substance is dissolved in dilute hydrochloric acid. The purity of the material used was verified in some cases by analysis of the reaction products. The above results together with others quoted (without references) lead to the conclusions that heats of formation of the oxides, hydrides, nitrides, and amides decrease with rise of atomic weight and that lithium occupies from the thermochemical point of view a position between calcium and strontium. The authors point out that lithium and barium easily yield amides and stable imides by direct action of the metal on ammonia, whilst the calcium and strontium compounds are only obtainable indirectly by decomposition of the corresponding nitride, which is a matter of some difficulty. A comparative table embodying both original and quoted results is given. H. J. E.

Heats of Vaporisation of Mercury and Cadmium. MAYOR F. FOGLER and WORTH H. RODEBUSH (*J. Amer. Chem. Soc.*, 1923, **45**, 2080—2090).—The importance of directly measured heat data as a supplement to vapour pressure data is discussed. The heat of vaporisation of mercury has been determined at 142°, and as a mean of 25 determinations the value 14490±50 cal. is obtained. The value calculated for 298·1° *K* is 14670±50 cal. A number of vapour pressure measurements have been made for cadmium at temperatures from 754·0° *K* to 867·6° *K* and from these data the value 25350±100 cal. is obtained as the latent heat of vaporisation at 594·1° *K*. The generalisations regarding the entropies of monatomic gases, and relating vapour pressures to heats of vaporisation are confirmed for zinc, cadmium, and mercury. J. F. S.

Study of Solutions at Different Temperatures. I. The Capacity for Heat of Aqueous Solutions of Hydrogen Chloride and Ammonia. M. S. VREVSKI and A. I. KAĬGORODOV (*J. Russ. Phys. Chem. Soc.*, 1923, **54**, 335—347).—The capacities for heat of aqueous solutions containing from 0·6 to 37·7% of hydrogen chloride, and from 1·47 to 32·3% of ammonia were determined at about 3°, 20°, 40°, and 60°. The determinations were carried out in a closed vessel to eliminate the effect of vaporisation at higher temperatures; the method of heating was electrical. The values obtained for the heat capacities at room temperature agree substantially with those of Thomsen, Marignac, and others.

The results of the investigation are expressed in the form of curves and it is shown that the heat capacity of hydrogen chloride solutions diminishes with increasing concentration, this being

observed at all temperatures. The heat capacity of ammonia solutions at low temperatures (2·4°) at first diminishes with increasing concentration and reaches a minimum at about 25% NH_3; it then begins to rise again. The curve for the same solutions at 20·7 shows a horizontal portion between 0 and 8% NH_3, the heat capacity being equal to that of pure water; it then increases for higher concentrations. At higher temperatures the heat capacity rises in proportion to the concentration.

Weak solutions of hydrogen chloride (below 3%) and ammonia (below 5%) exhibit a minimum of heat capacity similar to that observed for pure water by Callendar and Barnes (Kaye and Laby, "Chemical and Physical Constants," London, 1919, p. 56).

The heat capacity of hydrogen chloride solutions is lower than the calculated value, whilst the converse is observed for ammonia solutions. G. A. R. K.

Study of Solutions at Different Temperatures. II. The Heat of Solution of Hydrogen Chloride and Ammonia at Different Temperatures. M. S. Vrevski and N. N. Zavaricki (*J. Russ. Phys. Chem. Soc.*, 1923, **54**, 348—360).—The molecular heats of solution of hydrogen chloride and ammonia in water were determined at various temperatures. The method used consisted in the direct absorption of the gas in water, carried out in several stages; this is shown to be more accurate than the method of dilution.

It is found that the heat of solution rises rapidly in strong solutions, less so in weak solutions. With rise of temperature the heat of solution of hydrogen chloride rises, whilst that of ammonia diminishes. The heat of solution of hydrogen chloride at all temperatures increases with dilution; that of ammonia is remarkably constant for all concentrations below 12 or 15%.

G. A. R. K.

Study of Solutions at Different Temperatures. III. The Determination of the Density and Composition of the Vapour of Aqueous Solutions of Hydrogen Chloride and Hydrogen Bromide at Various Temperatures. M. S. Vrevski, N. N. Zavaricki, and L. E. Scharlov (*J. Russ. Phys. Chem. Soc.*, 1923, **54**, 360—375).—Using a specially constructed apparatus, the pressure and composition of the vapour in equilibrium with aqueous solutions at various temperatures were determined. Dry nitrogen was bubbled through the solution under investigation and the amount of water and acid carried away estimated. It is shown that the total vapour pressure of the solution diminishes with increasing concentrations of acid and reaches a minimum, then rises again; this minimum is more marked in solutions of hydrogen bromide and is greatest at low temperatures.

The partial pressure of the acids greatly depends on the concentration of the solution and is practically zero for solutions containing less than 10 % HCl and 20 % HBr at 19·9°. With rising concentration, the partial pressure rises rapidly and for solutions

containing more acid than the constant-boiling mixture the vapour consists of pure acid, the curve expressing the composition of the vapour rising very steeply.

A rise of temperature causes an increase in the partial pressure of the acid in solutions weaker than the constant-boiling mixture, whilst the converse is observed in stronger solutions; the effect of the temperature appears to be greatest for strong solutions. The experimental data referring to the composition of constant-boiling mixtures agree with the older data in the literature.

The results are shown to support the authors' view that for solutions the vapour pressure curve of which shows a minimum, the composition of the vapour and that of the constant-boiling mixture changes in opposite directions with change of temperature.

G. A. R. K.

Study of Solutions at Different Temperatures. IV. The Vapour Density and Heats of Formation of Solutions of Gases. M. S. VREVSKI (*J. Russ. Phys. Chem. Soc.*, 1923, **54**, 376—401).—A theoretical paper in which the results obtained in the three preceding papers are discussed from a mathematical point of view.

G. A. R. K.

Titrimetric Method for the Estimation of Density by Means of Floating Bodies. DOEMENS (*Svensk. Bryggmästare-Tidning*, 1923, 1; *Z. Ges. Brauwesen*, 1923, **46**, 23—29; from *Chem. Zentr.*, 1923, ii, 1201).—A method for the estimation of the density of a liquid consists in the addition of water to a known volume of the liquid until a glass float of known density sinks to the bottom of the vessel containing the liquid. G. W. R.

Piezochemical Studies. XXI. Calculation of the Coefficient of Compressibility. A. L. TH. MOESVELD (*Z. physikal. Chem.*, 1923, **105**, 442—449; cf. this vol., ii, 537).—A theoretical paper in which a method is described whereby equations may be deduced which enable the pressure relationship of the mean and actual compressibility to be calculated. For amyl alcohol, the two equations are: $\beta_m = 101{\cdot}5 - 36{\cdot}3\times10^{-9}p + 7{\cdot}47\times10^{-12}p^2$, and $\beta_w = 101{\cdot}5 - 72{\cdot}6\times10^{-9}p + 22{\cdot}41\times10^{-12}p^2$, where β_m and β_w are the mean and true compressibilities, respectively, and p is the pressure. The calculated and observed values are in good agreement. J. F. S.

Piezochemical Studies. XXII. Compressibility of Mixtures of Alcohol and Water. A. L. TH. MOESVELD (*Z. physikal. Chem.*, 1923, **105**, 450—454; cf. preceding abstract).—The mean compressibility of various mixtures of water and ethyl alcohol at 25° has been determined over the pressure range 0—1,500 atm. An equation has been evolved, which represents the mean compressibility of these mixtures as a function of the pressure, and also equations which represent the mean compressibility as a function of the concentration over the same pressure range. Tables of the experimental and calculated compressibilities are given which show a good agreement between the two sets of values. The

mean compressibility in terms of concentration is given by the following equations for the pressure ranges indicated: $10^6\beta_c^0 = 44{\cdot}5 - 0{\cdot}5443c + 0{\cdot}01754c^2 - 0{\cdot}06585{\cdot}10^{-3}c^3$; $10^6\beta_c^{0-500} = 42{\cdot}2 - 0{\cdot}4514c + 0{\cdot}01395c^2 - 0{\cdot}05234{\cdot}10^{-3}c^3$; $10^6\beta_c^{0-1000} = 39{\cdot}4 - 0{\cdot}3457c + 0{\cdot}01049c^2 - 0{\cdot}03773{\cdot}10^{-3}c^3$; $10^6\beta_c^{0-1500} = 37{\cdot}1 - 0{\cdot}3253c + 0{\cdot}00962c^2 - 0{\cdot}03762{\cdot}10^{-3}c^3$.
J. F. S.

Relation between Young's Modulus and Atomic Volume. Albert Portevin (*Compt. rend.*, 1923, **177**, 634—636).—An equation recently given by Peczalski (*ibid.*, **176**, 500), connecting Young's modulus (E) and atomic volume, is identical with that given by Fessenden (*Chem. News*, 1892, **66**, 206). The latter equation held for the common metals, but is useless where the value of E is high (rhodium tantalum and tungsten). In these cases, more satisfactory results are obtained with the equation $E = kT^a/V^b$, where T=absolute temperature, and a and b are, respectively, about 1 and 2. The various equations connecting coefficients of elasticity (modulus of compressibility, etc.) with surface tension, cubic expansibility, and specific heat are obviously simply modifications of the above type of formula. Some calculations are made (of E) for various minerals, using existing compressibility data. E. E. T.

Velocity of Sound in Nitrogen Tetroxide. A Lower Limit of its Velocity of Dissociation. E. Grüneisen and E. Goens (*Ann. Physik*, 1923, [iv], **72**, 193—220).—The velocity of sound in nitrogen tetroxide has been measured at various pressures and temperatures by Thiessen's method of closed cylindrical resonators. It is shown that up to frequencies of the order 15,000 sec.$^{-1}$ there is no indication that the velocity of sound depends on the frequency, as should be the case if the time required for setting up the dissociation equilibrium were comparable with the vibration period of sound. The absolute value of the velocity of sound agrees much better with the assumption that the time required for the setting up of a dissociation equilibrium is small in comparison with the vibration period. It can be stated from the most exact measurements at 25° and 760 mm. that the velocity constant of the decomposition, k, under the experimental conditions is certainly larger than 10,000. That is, every molecule of nitrogen tetroxide dissociates on the average at least once in every 10^{-4} sec. J. F. S.

Capillary Phenomena manifested at Surface of Separation of Water and Liquid Vaselin in Presence of Fatty Acids and Alkalis. René Dubrisay and Pierre Picard (*Compt. rend.*, 1923, **177**, 589—591; cf. A., 1918, ii, 368).—Alkali carbonates, like alkali hydroxides, diminish the interfacial tension between liquid vaselin and water, although to a much less extent. Alkali hydrogen carbonates have a slighter effect still. Neutral salts decrease the interfacial tension between mixtures of liquid vaselin and oleic acid and dilute soap solution, probably owing to their decreasing the solubility of soap and thus favouring its separation at the surface of separation. E. E. T.

Separation of Gas Mixtures by Diffusion into Steam under Pressure. FRANZ FISCHER, HANS SCHRADER, and ALBERT JAEGER (*Brennstoff-Chem.*, 1923, **4**, 289—296).—The gas mixture and steam are passed in opposite directions on either side of a porous earthenware division, and thence, through water condensers, to gas receivers. The best separation of light and heavy constituents is obtained with a medium gas and steam velocity and a relatively low steam pressure. Similar results are obtained by replacing the earthenware division by a layer of Raschig rings. For example, an illuminating gas containing 44—45% of hydrogen gave a diffusate containing 70—74% of hydrogen, and this was increased by a second diffusion to 95%. Using a diffusion zone of sand or a large number of narrow tubes, rather less satisfactory results are obtained. [Cf. *J.S.C.I.*, 1923, Nov.] W. T. K. B.

Calculation of Molecular Weights of Associated and Non-associated Liquid from the Critical Data. W. HERZ (*Z. Elektrochem.*, 1923, **29**, 394—395).—A theoretical paper in which it is shown that Berthelot's formula, $M=11{\cdot}4dT_k/p_k(2-T/T_k)$, yields at low temperatures fairly accurate values for the molecular weights of non-associated liquids and absolutely correct values at high temperatures. In the case of associated liquids, the molecular weights calculated by this formula are considerably too large at ordinary temperatures and only at very high temperatures are accurate figures obtained. Associated and non-associated liquids pass gradually into one another. J. F. S.

Mechanical Theory of Solutions. C. DIETERICI (*Ann. Physik*, 1923, [iv], **72**, 241—264).—A theoretical paper in which, by means of an empirical approximation, the author demonstrates the applicability of van der Waals's internal pressure equation to liquids, without making any assumptions with regard to van der Waals's quantities π and b. The author considers that the statement, that in the liquid phase of pure liquids over a wide range of temperature and pressure a constant value of the volume correction is always obtained, and that this same value of the volume correction is again found for all solutions in which no association or compound formation takes place, is fully confirmed on the mechanical basis considered. Further, the dimensions of cohesion pressure and its dependence on volume and temperature are also confirmed on the same basis. J. F. S.

Selective Solvent Action by the Constituents of Aqueous Alcohol. II. The Effect of some Alcohol-soluble Semi-solutes. ROBERT WRIGHT (T., 1923, **123**, 2493—2499).

The Increased Solubility of Phenolic Substances in Water on Addition of a Third Substance. CHARLES REYNOLDS BAILEY (T., 1923, **123**, 2579—2590).

Furthering of the Separation of Crystals and Gases from Supersaturated Solutions by Means of Fresh Surfaces and other Causes. R. FRICKE and C. ROHMANN (*Z. Elektrochem.*, 1923, 29, 400—402).—From a large number of experiments with super-

saturated solutions of potassium hydrogen tartrate it has been shown that the formation of a fresh surface or a surface partly separated from its surface film favours the separation of crystals. The effect of rubbing the vessel walls with a glass rod appears therefore to act in this way by forming a fresh surface. From a large number of experiments on solutions saturated with carbon dioxide, it is shown that the formation of a fresh surface also causes the separation of the gas, but here the nature of the substances in the surface is of importance, for some organic substances are active even with old surfaces, whilst others are not active. The presence of bubbles of another gas also favours the separation of the gas. J. F. S.

The Alleged Anomalous Reflection of *X*-Rays in Crystals. RALPH W. G. WYCKOFF (*Amer. J. Sci.*, 1923, [v], **6**, 277—287).—The "X-peak reflections," recorded by G. L. Clark and W. Duane (this vol., ii, 468) from spectrometric observations on potassium iodide, are not confirmed by Laue photographs taken through the cube faces of crystals of this salt, there being no spots developed in the required positions. The photographs conform completely with the sodium chloride arrangement of the atoms; and the only anomalous effect to be observed is a slight hazy diffraction quite close to the central spot, due, perhaps, to distortion in the crystal or to "asterism." L. J. S.

The Law of Distribution of Particles in Colloidal Suspensions with Special Reference to Perrin's Investigations. II. ALFRED W. PORTER and J. J. HEDGES (*Trans. Faraday Soc.*, 1923, **19**, 1—3).—In an emulsion of paraffin in distilled water, made by shaking the two liquids together for some hours and filtering, the change in concentration occurs at the bottom of the vessel and an increase of concentration takes place towards the surface of the liquid. The concentration n varies with the depth y according to the equation $\log_e n/(1-bn)+1/(1-bn)=Ky+A$, the values of the constants A, b, and K being, respectively, 83·23, $9{\cdot}7\times10^{-7}$, and -235. A. R. P.

The Penetration of Electrolytes into Gels. V. Diffusion of Mixtures of Chlorides in Gels. WALTER STILES (*Biochem. J.*, 1923, **17**, 530—534).—There is no antagonism between the chlorides employed in regard to their diffusion through agar and gelatin. The rate of diffusion of mixed chlorides is a little higher than would be expected from the values of the coefficients of diffusion of the respective salts in pure solution. S. S. Z.

Water-line Corrosion. KENNETH M. WATSON (*Trans. Amer. Electrochem. Soc.* [advance copy], 1923, 195—202).—Experiments have been carried out to ascertain the cause of water-line corrosion. Strips of zinc, copper, and brass were partly submerged in various corrosive liquids such as hydrochloric acid and solutions of sodium chloride, potassium nitrate, ammonium nitrate, calcium chloride, chromic, formic, acetic, phosphoric, hydrofluoroboric, and hydrofluorosilicic acids, and the conditions under which water-line corrosion occurs investigated. The results indicate that although the de-

polarising effect of oxygen is necessary for the corrosion of many metals in certain solutions, the contact of air with the upper surface of a liquid is never directly responsible for the occurrence of water-line corrosion. This phenomenon is caused by the slow downward flow of the heavier film of corrosion products along the surface of the metal, which draws in at the upper surface of the liquid a fresh supply of solution. Since all the metal except that at the surface of the liquid is in contact with partly exhausted solution, corrosion is most rapid at the water line. Although there is an even greater circulation of solution down the face of anodes used in the plating and refining of metals, water-line corrosion does not occur. In this work, the rate of corrosion is determined by the distribution of current over the anode surface, which depends on Ohm's law, and is only slightly affected by the amount of corrosion products contained in the film of solution that touches the anode. J. F. S.

The Distribution of Normal Fatty Acids between Water and Benzene. FREDERICK STANLEY BROWN and CHARLES E. BURY (T., 1923, **123**, 2430—2434).

The Liesegang Phenomenon—an Historical Note. J. R. I. HEPBURN (*Nature*, 1923, **112**, 439).—A claim for priority on behalf of Ord ("The Influence of Colloids upon Crystalline Form and Cohesion," London, 1879) over Liesegang in respect of the discovery of the phenomenon of stratified precipitation in gels. A. A. E.

A Method of Measuring the Velocity of Very Rapid Chemical Reactions. H. HARTRIDGE and F. J. W. ROUGHTON (*Proc. Roy. Soc.*, 1923, [*A*], **104**, 376—394).—A form of apparatus is described suitable for measuring the velocities of very rapid chemical reactions, such as the velocities of unimolecular reactions of which the half reaction is completed in as short a time as 1/300 sec. The fluids to be mixed are brought together at a high velocity within a restricted space by forcing them under considerable pressure through jets entering the space tangentially. The mixture thereafter flows with uniform velocity within a glass tube in such manner that estimations of the composition of the fluid at any cross section of the tube can be made by measuring the colour opacity, spectral absorption, optical activity, etc., of the fluid thereat. By using as fluids to be mixed $N/10$-solutions of sodium hydroxide and hydrochloric acid, the former being coloured with phenolphthalein, it is shown that with rates of flow through the observation tube equal to 400 cm. per sec., not more than 1% of the fluid remains unmixed. Various factors (nature of the flow in the observation tube, specific gravities of the liquids, surface tension) which might possibly influence the results obtained are discussed, and their effects shown to be negligible. J. S. G. T.

Mechanism of the Reduction of Permanganate and its Physico-chemical Basis. V. Mechanism of the Reduction of Manganate and its Dependence on the Alkalinity. JOSEF HOLLUTA (*Z. physikal. Chem.*, 1923, **106**, 276—294; cf. A., 1922, ii, 448, 628, 700, 771).—The reduction of manganate by formate

has been investigated in respect of its relation to the hydroxyl-ion concentration. It is shown that the velocity coefficients at low hydroxyl-ion concentrations change in inverse proportion to the square root of the hydroxyl-ion concentration. The effect of the hydroxyl-ion concentration on the velocity constant and on the pressure of oxygen liberated from the manganate is strictly in accord with the theory. It is shown to be probable that hydrated derivatives of manganese peroxide are the end-product of the reduction of manganate at high hydroxyl-ion concentrations. These compounds have a salt-like character. The importance of the adsorptive properties of the precipitated products on the further course of the reaction is discussed, and it is shown that in many cases a further reduction of the quadrivalent manganese takes place, which disturbs the normal course of the reaction when its velocity is very small. The retarding effect of low concentrations of hydroxyl-ion is overcome by an accelerating action at high alkali concentration which is found to be directly proportional to the hydroxyl-ion concentration. J. F. S.

Velocity of Formation of Chloride from Chloroform and Alkali. E. ABEL (*Z. Elektrochem.*, 1923, **29**, 391—394).—The velocity of formation of potassium chloride from potassium hydroxide and chloroform in ethyl alcohol solution at 25° has been investigated. The results show that the velocity is proportional to the chloroform concentration, but it is not proportional to the alkali concentration. The velocity increases much more rapidly than the concentration of alkali in the sense that starting with very dilute alkali solutions the apparent order of the reaction with respect to alkali is unity, but this increases with increasing alkali concentration. J. F. S.

The Velocity of Reaction in Mixed Solvents. VI. The Velocity of Saponification of certain Methyl Esters by Potassium Hydroxide in Methyl Alcohol–Water Mixtures. WALTER IDRIS JONES, HAMILTON MCCOMBIE, and HAROLD ARCHIBALD SCARBOROUGH (T., 1923, **123**, 2688—2698).

Rate of Hydrogenation of Cinnamic and Phenylpropiolic Acids. ERIC KEIGHTLEY RIDEAL (*Trans. Faraday Soc.*, 1923, **19**, 90—97).—The mechanism of the hydrogenation of sodium cinnamate and sodium phenylpropiolate in aqueous solution in the presence of a palladium sol stabilised with gum arabic has been examined. In the presence of sufficient catalyst, the rates at which $M/10$-solutions of the salts are hydrogenated are practically the same and proportional to the square of the shaking speed within very wide variations, the reaction velocity being of the zero order. For small quantities of catalyst, the reaction velocity is proportional to the palladium concentration, independent of the concentration of the salt within limits, and, above certain critical limits, of the shaking speed, but the rate of hydrogen absorption by the phenylpropiolate is twice that by the cinnamate. The reaction velocity in all cases depends on the age of the sol; with freshly prepared sols, the

curve is of the zero order practically throughout the reaction. As the age of the sols increases the proportion of the curve of zero order becomes gradually less, the reaction finishing as one of the first order, until with very old and inactive sols the reaction throughout is of the first order. It is shown that the salt is adsorbed on the surface of the catalyst together with the hydrogen, and that it remains adsorbed until completely hydrogenated; this explains the fact that both salts are hydrogenated at the same rate, the phenylpropiolate taking up 2 mols. of hydrogen whilst the cinnamate is taking up 1 mol. A. R. P.

Piezochemical Studies. XXIII. Influence of Pressure on the Velocity of Reaction in Homogeneous Liquid Systems. V. Liquid Mixtures. A. L. TH. MOESVELD (*Z. physikal. Chem.*, 1923, **105**, 455—471; cf. this vol., ii, 740).—The velocity reaction between 0·01*N*-sodium hydroxide and 0·01*N*-ethyl *o*-methoxycinnamate in 31 and 42·5 weight % ethyl alcohol at 25° has been determined at 1, 500, 1,000, and 1,500 atm. pressure. It is shown that in both solvents the velocity increases considerably as the pressure is increased. At 1,500 atm., the velocity constant is 2·34 and 2·15 times as large, respectively, as under 1 atm. pressure. The pressure coefficient of the velocity increases very much with increase in pressure. J. F. S.

The Kinetics of Hæmoglobin. II. The Velocity with which Oxygen Dissociates from its Combination with Hæmoglobin. H. HARTRIDGE and F. J. W. ROUGHTON (*Proc. Roy. Soc.*, 1923, [*A*], **104**, 395—430).—In continuation of previous work (this vol., ii, 229), the authors have determined the rate of reduction of oxyhæmoglobin by sodium hyposulphite, employing for this purpose the form of apparatus described in a previous paper (this vol., ii, 744). The chemical composition of the solution at any section of the observation tube through which it flowed from the mixing chamber was determined by means of the reversion spectroscope (this vol., ii, 105), using an auxiliary trough containing a solution of hæmoglobin saturated with carbon monoxide. It was shown that the velocity of reduction due to sodium hyposulphite was practically identical with that found when the reduction was effected by suitable physical means. For this and other reasons, it was concluded that the dissociation was not appreciably retarded by any back reaction between oxygen and reduced hæmoglobin. The results obtained indicate that the reduction of oxyhæmoglobin is a unimolecular reaction obeying the law of mass action. Hydrogen-ion concentration has a marked effect on the velocity of the reaction. On the alkaline side of p_H 7·7, the velocity is constant, and on the acid side of p_H 6·3, the velocity is probably also constant, having a value about seven times that corresponding with p_H 7·7; between p_H 6·3 and p_H 7·7 there is a gradual change from the one rate to the other. The interpretation of the p_H effect and the legitimacy of adopting a single velocity equation are discussed in detail. The effect of temperature on the velocity constant is in accord with Arrhenius's equation (A., 1889, 1103). At p_H 6·3

and p_H 7·7, the value of the temperature coefficient of the velocity of reaction is 3·8. At the low concentrations of hæmoglobin used, variations in the salt content of the solution are without effect on the velocity of reduction. J. S. G. T.

Catalysis by the Action of Subdivided Metals. I. Heat of Adsorption of Hydrogen on Finely-divided Nickel. B. Foresti (*Gazzetta*, 1923, **53**, 487—493).—The author obtains values lying between 10957·6 and 11977·2 cal. for the molecular heat of adsorption at 0° of hydrogen at constant volume by nickel reduced from its oxide at 300°. The mean value, 11430·8 cal., is in satisfactory agreement with that calculated by Rideal (T., 1922, **121**, 309). The amount of the gas adsorbable by the metal varies with different samples of nickel, and is considerably affected by the extent of the vacuum attained during the evacuation of the metal prior to the experiment and by the period of contact of the metal with the gas at reduced pressure. The values found by Gauger and Taylor for the heat of adsorption of hydrogen (this vol., ii, 398) are lower than the true values. T. H. P.

Behaviour of certain Metals as Catalysts. II. C. Sandonnini (*Gazzetta*, 1923, **53**, 453—461).—Investigation of the changes occurring in hydrogen-oxygen mixtures at various temperatures and in presence of either reduced nickel, or purified sugar carbon containing 0·65% of ash, or mixtures of these two catalysts (cf. A., 1922, ii, 557) shows that carbon does not act on detonating gas as an energetic catalyst and that at 300—350° it absorbs oxygen, which at higher temperatures it gives up as carbon monoxide and dioxide. Nickel, however, exerts marked catalysing influence on the union of hydrogen and oxygen and also on the reactions resulting in the oxidation of the carbon. Formation of hydrocarbons was observed in none of the experiments.

T. H. P.

Catalytic Decomposition of Hydrogen Peroxide in a Bromine-Bromide Solution. II. Rate Measurements in Dilute Solutions and in the Absence of Sulphate, and their Interpretation as a Function of the Activity Product of Hydrobromic Acid. Robert S. Livingston and William C. Bray (*J. Amer. Chem. Soc.*, 1923, **45**, 2048—2058; cf. this vol., ii, 473).—A continuation of previous work in which the catalytic decomposition of hydrogen peroxide in solutions of sulphuric acid and potassium bromide, more dilute than previously examined, has been investigated at 25° with the object of determining the reason why the value of *k* increased as the acid concentration was decreased below 0·2*N*. It is shown that the steady state rate of the bromine-bromide catalysis approaches a definite finite value as the concentration of the sulphuric acid is indefinitely decreased. The steady state rate has also been measured in solutions of hydrobromic acid, hydrobromic acid-perchloric acid, hydrobromic acid-potassium bromate, hydrobromic acid-barium bromide, and perchloric acid-potassium bromide. The rate constants obtained

from measurements in these various solutions are all slightly larger than those obtained in sulphuric acid solutions more concentrated than $0{\cdot}2N$. At the steady state in hydrobromic acid and hydrobromic acid–perchloric acid solutions of ionic strength less than 0·25 and in many of the experiments in the absence of sulphate, the rate of decomposition of the peroxide is represented by the following expression within the limits of experimental error, 1%—2%: $-d(H_2O_2)/dt=0{\cdot}0437(H_2O_2)(H^{\cdot})(Br')\gamma^2_{HBr}$. The activity coefficient, γ_{HBr}, in solutions containing sulphuric acid and potassium bromide has been estimated from the rate measurements in these solutions on the assumption that the above equation is true. The application of the "activity rate" hypothesis and of Brönsted's hypothesis to the present experiments is discussed. J. F. S.

Catalytic Dehydroxidation of Formic Acid. II. ERICH MÜLLER and JOHANNES KEIL (*Z. Elektrochem.*, 1923, **29**, 395—399; cf. A., 1922, ii, 558).—The catalytic decomposition of formic acid into carbon dioxide and hydrogen by means of metallic osmium is connected very largely with the degree of dispersion of the metal. The necessary degree of dispersion is obtained when a compound of osmium (osmium tetroxide, potassium osmate, or potassium chloro-osmate) is acted on by formic acid itself. The osmium thus produced enters in the highly dispersed condition with the acid practically in statu nascendi, and exhibits a hitherto unobserved catalytic action. The catalyst loses its activity rapidly, because the degree of dispersion is reduced. The retardation of the catalysis can be largely prevented by the addition of a protective colloid, such as gelatin. The catalysis of the decomposition of formic acid by osmium shows a large induction period which is removed very largely by the presence of a little metallic osmium. The catalytic decomposition of formic acid in the presence of an osmium compound and gelatin takes place more easily, more certainly, and more completely than in the presence of metallic osmium which has been prepared by the reduction of the tetroxide by means of hydrogen. J. F. S.

Isotopes. F. W. ASTON (*Chemistry and Industry*, 1923, **42**, 935).—Measurements of the masses of the atoms or isotopes of elements not hitherto examined have now been made by a new method. The following elements are found to be simple: scandium, 45; titanium, 48; vanadium, 51; chromium, 52; manganese, 55; cobalt, 59; strontium, 88; yttrium, 89. Gallium has two isotopes, 69 and 71, germanium has three, 74, 72, and 70, and silver has two, 107 and 109. The atomic masses and isotopes of the first forty elements and a few others are now known. With the exception of nitrogen, every odd element has an odd atomic weight, and no atomic weight, excepting that of hydrogen, is less than twice the atomic number. E. H. R.

A Calculation of the Atomic Weights of Isotopes. A. S. RUSSELL (*Nature*, 1923, **112**, 588—589; cf. this vol., ii, 719).—Rules have been formulated from radioactive data whereby the

atomic weights of the principal isotopes of common and radioactive elements may be calculated. It is deduced solely from radioactive evidence that isotopes probably do not differ by more than 8 units of atomic weight; that only end-products of radioactive series or radio-elements emitting α-particles should be considered when a comparison is made between common and radioactive isotopes; that all elements are limited to two isotopes of odd atomic weight, differing by 2 units only; that elements of odd atomic number have odd isotopes only, the lighter being likely to be the more stable and abundant; that even elements may have both even and odd isotopes, the former usually being at least twice as numerous as the latter, and the lightest or heaviest not being odd; that isobares of common elements may be of even atomic weight only; that an element of atomic number [?] $4n+3$ has an isotope of atomic weight $4n+1$ and vice versa; and that an even element has always one isotope a unit of atomic weight higher than one of the isotopes of the element next below it. The rules, some of which have already been formulated by Aston, do not apply in their entirety to elements below nickel and cobalt. Branching according to an unknown plan, and indecisive radioactive evidence concerning which mass-numbers are unstable and which are possible isobares, prevent the determination by calculation of all the isotopes of every element. The atomic weights of isotopes calculated in this way are quoted, and shown to agree closely, although not absolutely, with Aston's results. The complexity of an element appears to be a simple function of the atomic number $16n$. It is considered probable that elements of atomic numbers $16n+7$, $16n+10$, and $16n+11$ are simple; that $16n+3$, $16n+5$, $16n+13$, and $16n+15$ have two isotopes; that $16n+8$, and $16n+14$ have no odd isotopes; and that $16n$, $16n+2$, and $16n+12$ have odd isotopes A. A. E.

The Periodic Law. P. I. PETRENKO-KRITSCHENKO (*J. Russ. Phys. Chem. Soc.*, 1923, **54**, 447—454).—A theoretical paper in which certain seemingly anomalous chemical facts such as the effect of accumulation of hydroxyl groups in organic acids, the heats of combination of elements with oxygen, etc., are discussed, and an attempt is made to demonstrate an element of periodicity in connexion with these facts. The arguments do not lend themselves to condensation. G. A. R. K.

Active Cross-section of Gas Molecules for Slow Electrons. II. CARL RAMSAUER (*Ann. Physik*, 1923, [ii], **72**, 345—352; cf. A., 1921, ii. 324).—In the earlier paper (*loc. cit.*), methods were described for the determination of the total active cross-section of gaseous molecules for slow electrons as a function of the velocity of the electrons. Using the same method, the work has been continued with krypton and xenon. It is shown that whilst for hydrogen, nitrogen, helium, and argon the active cross-section and the absorbing cross-section are practically the same for the smallest electron velocities, there are indications that these two quantities for argon, krypton, and xenon commence to differ for velocities between 30 and 70 volts; the divergence between the two commences

sooner the larger the atomic number. All inactive gases show the same peculiarity in comparison with the other gases (nitrogen, hydrogen, and carbon dioxide) investigated namely that the active cross-section reaches a maximum and then falls with decreasing electron velocity. The gases argon, krypton, and xenon exhibit the above peculiarity very markedly in two respects; the active cross-section increases to a maximum which is four to five times as large as the kinetic gas cross-section and then falls to one-seventh of the kinetic cross-section for velocities of 0·75 volt. Below this velocity no definite statements can be made. The gases neon, argon, krypton, and xenon show a definite progression in respect of the position and height of their maxima; with increasing atomic number (10, 18, 36, 54) the maxima increase strongly (active cross-section in $cm.^2/cm.^3$ for 0° and 1 mm. mercury, 13, 82, 98, 141), and in addition are displaced to smaller electron velocities ($volt_{max.}$=25, 13·2, 11·3, 6·4). J. F. S.

Structure and Deformation of Electron Sheaths and their Significance for the Optical and Chemical Properties of Inorganic Compounds. K. FAJANS (*Naturwiss.*, 1923, **11**, 165—172; from *Chem. Zentr.*, 1923, iii, 2—3).—The author discusses the hypothesis that in the activation of ions, and consequently of atoms and molecules, the deformation of electron sheaths is an important factor.

[With G. JOOS.]—Optical properties are a measure of deformability. The deformation of inert gas electron sheaths increases with increase of atomic size, anions being more deformable than kations, particularly when associated with a hydrogen nucleus.

[With H. BEUTLER.]—It appears from colour phenomena that the electron path of the anion is deflected to the kation. This is illustrated by compounds of copper. With kations of the inert gas type, the colour effect is the greater the more highly charged is the kation and the smaller its radius.

[With A. SCOTT.]—A deformed anion will approach more closely to a kation than will a rigid anion of equal magnitude. This is illustrated by data for heats of formation and lattice energies of salts. In general, the lattice energy of a salt with a heavy metal (without inert gas sheath) exceeds that of a salt of an equally charged kation of the inert gas type the more deformable the associated anion is.

[With A. HOLSTAMM.]—The behaviour of alkali metal halides shows that the ions compete for water in solutions. When acids dissociate in aqueous solution it is supposed that the hydrogen-ion associates with water to form H_3O^+.

It is concluded from a study of the colour of the halides of titanium and silicon and of other compounds that extreme deformation results in a compacting rather than a loosening of electron paths. G. W. R.

Co-ordination and the Electrons. T. MARTIN LOWRY (*Chemistry and Industry*, 1923, **42**, 1004—1007).—The factors which have led to delay in the universal acceptance of Werner's

theory of co-ordination are discussed. The view that the development of conjugated rings is an important factor in promoting co-ordination is maintained, in view of the strong experimental evidence on which it is based.

Kinetic Foundation for Chemical Affinity. J. K. SYRKIN (*Z. physikal. Chem.*, 1923, **106**, 243—254).—A theoretical paper in which it is shown that a kinetic representation of chemical affinity can be developed from considerations of molecular collisions on the assumption that not all the molecules are active, but only a portion of them, which is determined by a definite energetic condition furnished from considerations of statistical mechanics. An equation for chemical equilibrium is deduced on this basis and has the form $\log k = \log_e n_1!n_2!/n_1'!n'_2! - Q/RT - \Sigma n$, where k is the equilibrium constant, Q is the heat change of the reaction, n_1 and n_2 are the number of molecules of each kind reacting, n'_1 and n'_2 are the number of molecules of each product, and n is the total number of reacting molecules, $n=n_1+n_2$. A kinetic equation is developed for reactions of any given order (2 or higher); this has the form $K=(\sqrt{0(8)\pi R}\sigma^{n-1}/n_1!n_2!r)N_0^{n-1}\sqrt{(n_1/M_1+n_2/M_2+\ldots)/(n_1+n_2)}\sqrt{T}e^{-q/RT}$, where K is the velocity constant, σ is the sphere in which collision can occur, r is the radius of the reaction sphere, M_1 and M_2 are the molecular weights, and the other symbols have their usual meanings or those given in the first equation. J. F. S.

Measure of Chemical Affinity. RUDOLF WEGSCHEIDER (*Z. physikal. Chem.*, 1923, **106**, 18—36).—A theoretical paper in which it is shown from a measure of affinity that it must be demanded that it shall depend on the momentary state of the system alone and not on the conditions under which the following change takes place. This condition is satisfied only by the measurement of the affinity from the maximum obtainable work reduced by that required for overcoming the external pressure. Consequently, the volume energy is not to be regarded as a constituent of the chemical energy, nor is the opposing pressure which stops a reaction a measure of the affinity. On the other hand, the work of mixing is only to be deducted when the mixing takes place independently of the reaction itself, but it must not be deducted for the chemical processes which occur in galvanic elements in which actually no mixing takes place. The affinity is dependent on the condition of the system and consequently can, in general, not be defined by any work done by a finite change, but only by the differential quotient. These views are expressed by equations and elaborated by means of definite examples. Here, among other things, a new method is used for proceeding from the unmixed reactants to the unmixed products in a chemical reaction. Previous definitions of affinity refer to processes leading to equilibria (reaction and opposing reaction). The author discusses whether or no the forces of a single reaction can be defined. J. F. S.

Early Greek Chemistry. J. R. PARTINGTON (*Nature*, 1923, **112**, 590).—Comments on Berthelot and Ruelle's "Collection des

anciens alchimistes grecs" and Stéphanidès's emendations thereof (*Rev. études grecques*, 1922, **35**, No. 162). A. A. E.

Glass to Metal Joint. CYRIL H. MEYERS (*J. Amer. Chem. Soc.*, 1923, **45**, 2135—2136).—Glass to metal joints may be made by coating the metal part with tin or solder and cleaning the surface thoroughly with zinc chloride. The glass part is cleaned with chromic acid and water and then dried. The metal part is then heated until the solder or tin just melts and the glass, which has been previously warmed, slowly inserted. It is essential that the surfaces of both glass and metal should be clean and that the temperature reached in the soldering does not exceed that required to melt the solder. J. F. S.

A Simple Attachment for Gas Generators. L. SPIEGEL (*Ber.*, 1923, **56**, [*B*], 2068).—A device for attachment to the lower end of the tap funnel used in ordinary gas generators, to prevent a back-rush of gas through the tap. It consists of a U-tube with the longer leg closed except for a small hole at the top. The short limb is attached to the lower end of the dropping funnel by means of a well-greased ground joint. The result is that the U-tube becomes full of liquid, which effectually prevents a back-rush of gas. H. H.

Cellulose Acetate as a Material for the Preparation of Ultra-filters. R. FRICKE and P. KLEMPT (*Kolloid Z.*, 1923, **23**, 164—168).—Ultra-filters may be made from cellulose acetate as follows: A solution of cellulose acetate (3—10 g.) in a mixture of one volume of 96% ethyl alcohol and nine volumes of chloroform is poured uniformly on a glass plate and allowed to dry in the air. The plate and filter are then placed in 96% alcohol for a short time to dissolve out the last traces of chloroform. The filter is loosened at one side and stripped from the plate and preserved in cold water. Such filters are durable and of suitable density, they may be bent without breaking and are best used inside a filter-paper. A number of examples of the use of cellulose acetate filters is given in the paper. J. F. S.

Inorganic Chemistry.

Electrolytic Generator for Pure Hydrogen. VISCOUNT ELVEDEN and ERIC SINKINSON (T., 1923, **123**, 2715—2716).

The Low Temperature Activation of Hydrogen. ALLAN ERNEST MITCHELL and ABRAHAM LINCOLN MARSHALL (T., 1923, **123**, 2448—2457).

The Catalytic Decomposition of Hydrogen Peroxide Solution by Carbons prepared from Carbohydrates. J. B. FIRTH and F. S. WATSON (*J. Soc. Chem. Ind.*, 1923, **42**, 371—372T; cf. T., 1923, **123**, 1750).—The volume of oxygen liberated

from hydrogen peroxide by carbon from various carbohydrate sources was studied. When the samples of carbon were merely dried at 100°, it was found that those from cellulose and rice starch were moderately active; those from dextrin, inulin, and wheat starch were slightly active; whilst those from dextrose, lactose, lævulose, maltose, and potato-starch were practically inactive. Heating the carbons in a vacuum for two hours at 600° increased their catalytic activity in all cases. The increase was most marked in the case of inulin carbon, and least for potato-starch and lævulose carbons. Previous sorption and removal of iodine caused a marked increase in the activity in all cases except that of wheat-starch carbon. The increase in the activity of cellulose-carbon was especially striking. The relative bulk of a carbon is not a decisive factor in determining its activity. H. H.

Vapour Pressures and Crystal Lattices of the Hydrogen Halides. F. A. Henglein [with R. Roth and P. Andres] (*Z. Physik*, 1923, **18**, 64—69).—The following values, expressed in mm. of mercury, have been found for the vapour pressures of solid hydrochloric acid, liquid and solid hydrobromic acid, and solid hydriodic acid, at the respective temperatures (measured on the absolute scale) stated: HCl (solid): 161°, 122·2; 158·9°, 100·2; 156·7°, 82·6; 156·0°, 76·0; 149·7°, 40·2; 142·2°, 17·9; 121·0°, 0·891; 115·1°, 0·363; HBr (liquid): 208·7°, 869·9; 194·5°, 400·9; 187·3°, 255·9; (solid) 177·6°, 124·5; 161·2°, 28·2; 157·0°, 17·66; 156·0°, 16·0; 148·7°, 7·30; 144·1°, 4·03; HI (solid): 208·3°, 162·0; 194·7°, 68·0; 177·7°, 18·8. The author's results in the case of hydrobromic acid are not in agreement with those of McIntosh and Steele (A., 1904, ii, 533). The respective vapour pressures in mm. of mercury can be represented as a function of the absolute temperature by equations of the form $\log p=7{\cdot}5030-K/T^n$, the following being the respective values of K and n: HCl (liquid), 945·7, 1·0160; (solid), 1966·3, 1·1600; HBr (liquid), 1037·2, 1·0160; (solid), 2202·0, 1·1602; HI (liquid), 1197·3, 1·0160; (solid), 1435·9, 1·0496. The results indicate that as in the case of the halogens, the hydrogen halides form molecular lattices. Moreover, the crystal form of solid hydrogen iodide is different from that of hydrogen chloride and hydrogen bromide, and it is possible that at lower temperatures a second crystalline modification occurs. The following values of vapour pressure (in mm.) at the melting point characterise the respective molecular and ionic lattices:—molecular lattices: Cl, 8·9; Br, 44·1; I, 87·0; HCl, 125·2; HBr, 224·2; HI, 369; ionic lattices: KCl, KBr, KI, about 0·4. J. S. G. T.

Irregularities in the Rate of Solution of Oxygen by Water. H. G. Becker and E. F. Pearson (*Sci. Proc. Roy. Dubl. Soc.*, 1923, **17**, 197—200).—Measurements of the rate of absorption of oxygen at a still water surface show that, up to 60 or 70% of saturation, the absorption follows the same logarithmic law as if the water were kept continually mixed, but beyond this point wide irregularities occur. The causes determining the uniform

mixing in the early stages and its failure in the later stages of absorption have not been elucidated. E. H. R.

Recent Progress in the Production of Ozone with High Tension Discharges. FRANK E. HARTMAN (*Trans. Amer. Electrochem. Soc.* [advance copy], 1923, 295—306).—The paper deals with the production of ozone by the silent discharge methods. Data are given which show that the energy density of an ozoniser is a straight-line function of the cycles; and that the yield of ozone is a straight-line function of the energy density at atmospheric pressure. It is further shown that ozonising at high gas pressures is conducive to better cooling of the electrodes, thus making it possible to produce high concentrations of ozone with high energy densities. A relationship is also established between high gas pressures and the efficiency of an ozoniser. J. F. S.

Preparation of Ozone with a High Frequency Alternating Current. ALFRED STARKE (*Z. Electrochem.*, 1923, **29**, 358—364).—The author has made experiments to ascertain whether by increasing the frequency of the alternating current up to the value 10,000 it is possible to reach the increased theoretical intake of energy in an ozone tube without decreasing the energy yield, the ozone concentration, and the safety of the tube. Experiment shows that by using a frequency of 10,000 at constant voltage, about 200 times as much ozone can be produced in the same tube as with a frequency of 50. An unfavourable effect of the high frequency could not be found in connexion with the energy yield, the concentration of the ozone, or the safety of the tube; on the other hand, a slight influence of the frequency on the work factor was found. The work factor increases up to a frequency of 3,200, and then falls slightly. A calculation shows that the very high costs of a large ozone plant are considerably reduced by employing a high frequency alternating current. J. F. S.

Amorphous Sulphur in Flowers of Sulphur and its Transformation in the Preparation of Precipitated Sulphur. R. HUERRE (*J. Pharm. Chim.*, 1923, [vii], **28**, 223—232).—Amorphous sulphur insoluble in carbon disulphide, is converted into the soluble modification when heated at about 100° with an animal or vegetable oil, with a 10% solution of sodium sulphite, or with water alone. The insoluble sulphur does not dissolve in a cold 10% solution of sodium sulphite, and only a trace dissolves in the boiling solution. Amorphous sulphur is completely soluble in a cold aqueous solution of sodium sulphide, and from the solution the soluble modification is obtained by precipitation with an acid or even by extraction with carbon disulphide. W. T. K. B.

Action of Selenium Oxychloride on Various Metals and Metallic Oxides. WARD L. RAY (*J. Amer. Chem. Soc.*, 1923, **45**, 2090—2094).—Selenium oxychloride reacts with metallic copper at the ordinary temperature, forming a black substance which is a mixture of cuprous and cupric selenides. On continued action, the selenides are converted into anhydrous cupric chloride:—

$3Cu + 4SeOCl_2 = 3CuCl_2 + 2SeO_2 + Se_2Cl_2$. Anhydrous cupric chloride reacts with selenium oxychloride to form a green, crystalline acid selenite, $CuCl_2 + 3SeO_2 = CuSeO_3,SeO_2 + SeOCl_2$. The selenium oxychloride acts merely as a solvent for cupric chloride and selenium dioxide formed by hydrolysis of some of the oxychloride by moist air. Silver is changed successively into the selenide and chloride by the same reagent. The oxides of copper, silver, lead, nickel, cobalt, iron, antimony, bismuth, and tin are converted into chlorides by the action of selenium oxychloride and selenium dioxide is formed. J. F. S.

Equation of State for Pure Nitrogen, Gas Phase. LEIGHTON B. SMITH and ROBERT S. TAYLOR (*J. Amer. Chem. Soc.*, 1923, **45**, 2107—2124).—The *p.v.T.* relationship of pure gaseous nitrogen has been studied by the isometric method over the temperature range 0° to 200° and the pressure range 30—300 atms. The Keyes equation expresses the data obtained within the limits of experimental error. The equation obtained is $p_{atm.} = 2{\cdot}92855T/(v\text{-}\delta) - 1623{\cdot}63/(v+0{\cdot}2954)^2$, where $\delta = 0{\cdot}18683 - 0{\cdot}3113/v$. The weight of a litre of nitrogen at *N.T.P.* is calculated from the equation of state to be 1·2509 g., as compared with the generally accepted value, 1·2507 g. The compressibility coefficient at 0° is calculated and found to be 0·00061, as compared with 0·00056 from Otto and Holborn's equation and Rayleigh's work, and 0·00043 and 0·00044 from Chappius Maverick, respectively. J. F. S.

Nitrogen Fixation by Means of the Cyanide Process and Atomic Structure. L. HAMBURGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **26**, 480—485).—From consideration of atomic structure, it is deduced that for reactions which occur in the gas phase, the relation, critical energy supply/reaction temperature = constant, should hold good. For reactions of the type $MO = M + O$, there then exists the relation, ionisation potential of the metal (V)/absolute temperature of reaction $(T) = k$. This is found to be substantially true for the alkali and alkaline-earth metals. For reactions between compounds, however, *e.g.*, $MCO_3 = MO + CO_2$, the term ionisation potential cannot strictly be employed, because the electron which is to be ionised is probably already moving in a distorted orbit, so that an amount of energy less by V' than the ionisation potential of the free metal will be required to detach the electron completely. V' is termed the dislocation potential of the compound, and is probably nearly equal to its excitation potential (V''). It is found that, in accordance with this theory, $(V - V'')/T$ is practically constant for cyanising reactions. H. H.

The Glow of Phosphorus, and its Extinction by Moist Oxygen. LORD RAYLEIGH (*Proc. Roy. Soc.*, 1923, [*A*], **104**, 322—332).—The author has investigated the conditions determining the possibility of detaching the luminosity from a stick of glowing phosphorus by a blast of air, a phenomenon previously described by L. and E. Bloch (A., 1908, ii, 1032). It was found that the velocity of the blast necessary to effect such detachment increased

greatly with rise of temperature and decreased greatly with increase in the oxygen content of the air blast. Thus at 4°, the necessary velocity was increased 1,000 times by an increase of 1% in the oxygen content of the air blast employed. When the velocity of the blast was 100 cm. per sec. or more, the glow exhibited a tendency to cling to certain points at which depressions occurred on the phosphorus surface and from which the luminosity spread out fanwise. Extinction of the glow by an atmosphere of moist oxygen is regarded as the limiting case of slow propagation, and arises probably owing to failure of the catalytic action of the products of combustion of the phosphorus to effect propagation of the glow. Oxygen, present in excess, inhibits such catalytic action, possibly by a process of condensation analogous to that whereby the motion of ions produced in gaseous combustion is reduced. J. S. G. T.

Change of Realgar into Orpiment and the Analogous Behaviour of Arsenic Sulphide Sols. S. S. BHATNAGAR and B. LAKSHMAN RAO (*Kolloid Z.*, 1923, **23**, 159—164).—It is shown that the hydrosulphide-ion, SH′, and not the sulphide-ion, S″, is the active agent in the precipitation of metallic sulphides by hydrogen sulphide. The colloidal solutions of sulphides obtained in this way can be regarded as solutions of hydrosulphides. When a colloidal solution of arsenic sulphide is heated or when hydrogen is passed through it so that all the free and combined hydrogen sulphide is removed, the formula of the colloidal sulphide is not As_2S_3, but much more nearly As_2S_2 or AsS. It is shown that the action of heat on a red colloidal solution converts it into a yellow sol with the precipitation of sulphur, according to the equation $As_2S_2,xH_2S+xO=As_2S_3+xH_2O+(x-1)S$. When the content of combined hydrogen sulphide is small, no sulphur is precipitated. The action of light and heat consists mainly in the transformation of one variety into the other, and may be represented by the equation $As_2S_2+H_2S+O=As_2S_2,S+H_2O$. By analysis, measurement of density, and the absorption spectrum, it is shown to be likely that the red variety is identical with realgar and the yellow precipitate with orpiment, both in colour and in other properties. J. F. S.

Perborates. HEINRICH MENZEL (*Z. physikal. Chem.*, 1923, **105**, 402—441).—By means of freezing point and electrical conductivity measurements at 0°, it is shown that a combination between hydrogen peroxide and boric acid in aqueous solution cannot be substantiated, and in consequence the decomposition constant of perboric acid, $K=[H_2O_2][H_3BO_3]/[H_3BO_3,H_2O_2]$, must be exceedingly large. The effect of varying quantities of hydrogen peroxide on the equivalent conductivity of metaborate and borax solutions of various concentrations has been investigated. It is shown that with increasing concentration of hydrochloric acid and increasing additions of hydrogen peroxide the electrical conductivity is continuously decreased, which is to be regarded as due to the formation of many additive products with small degree of hydrolysis and small

mobility. Cryoscopic measurements with solutions of metaborates and borax in the presence of hydrogen peroxide show that the metaborate-ion and the more complicated ions from concentrated solutions of borax combine with hydrogen peroxide, and in the higher concentrations of metaborates a polymerisation of the simpler ions also takes place, since the osmotic concentration is smaller than that of the original metaborate solution. By means of partition experiments with amyl alcohol, the combination of hydrogen peroxide with the metaborate-ion is also demonstrated. These results taken together with the freezing-point measurements show that in 0·02—0·07M metaborate solutions containing hydrogen peroxide the simple ion $(BO_2,H_2O_2)'$ is in equilibrium with free metaborate and free hydrogen peroxide, whilst in concentrated solutions, polymerisation takes place and more than 1 mol. of hydrogen peroxide is combined with a single boron atom. In the case of the simple acid, H_3BO_3,H_2O_2, and its ion, BO_2,H_2O_2', it is found that the decomposition constant of perboric acid bears the same relation to the decomposition constant of its ion as the dissociation constant of perboric acid bears to the dissociation constant of boric acid. Since free perboric acid is not present to a measurable extent and its decomposition constant is very large, an apparent dissociation constant for perboric acid can be deduced from the equilibrium $H^{\cdot}+(BO_2H_2O_2)' \rightleftharpoons HBO_2+H_2O_2$, which has the form

$$[H^{\cdot}][BO_2,H_2O_2']/[HBO_2][H_2O_2]=K'_p,$$

and is equal to the quotient of the true dissociation constant of perboric acid and its decomposition constant, and therefore equal to the ratio between the dissociation constant of boric acid to the decomposition constant of the perborate-ion. From partition experiments, it is found that the decomposition constant, K_{zi}, of the perborate-ion at 0° is $2{\cdot}4\times10^{-2}$, and at 18°, $3{\cdot}3\times10^{-2}$ from which the apparent dissociation constant of perboric acid, K'_p is calculated to be $>1{\cdot}10^{-8}$ for 0° and $1{\cdot}7\times10^{-8}$ for 18°. Independently from the above, colorimetric measurements with dilute solutions give as the apparent dissociation constant of perboric acid $K'_p \simeq 2\times10^{-8}$ against the boric acid constant $K_B=5{\cdot}7\times10^{-10}$. Further, colorimetric measurements show that in the more concentrated solutions a greater reduction of alkalinity and affinity takes place, due to the formation of complicated acids, a fact which explains the evolution of carbon dioxide from mixtures of borax and hydrogen carbonates on the addition of hydrogen peroxide. J. F. S.

Vitreous Carbon. A Special Form of Crystalline Carbon. K. A. HOFMANN and CURT RÖCHLING (*Ber.*, 1923, **56**, [*B*], 2071—2076).—By exposing a heated, chemically inert surface to the luminous flame of some aliphatic hydrocarbons or halogenated compounds, a deposit of a hard, lustrous, crystalline form of carbon is obtained. The minimum temperature of the surface is 650°, and both the nature of the surface and the kind of compound used to carburet the gas are important. A steel surface, probably owing to the intermediate formation of metallic carbides, gives

only a deposit of graphitic carbon, whilst flames of burning benzene and naphthalene gave only amorphous, sooty carbon, or, at higher temperatures, graphitic carbon.

The vitreous form of carbon now described has a high density (d_4=2·07), is very pure (C=99·06%, H=0·48%), and has a low electrical conductivity ($\frac{1}{8}$—$\frac{1}{15}$ of that of Ceylon graphite, and $\frac{1}{3}$—$\frac{1}{8}$ of that of Acheson graphite). It is also very hard, that prepared at 900° having a hardness equal to that of quartz, at 1100° having a hardness equal to that of topaz, whilst that prepared at 1300° is harder than carborundum. It is considered to be a form intermediate between graphite and diamond, and its *X*-ray spectrum shows characteristic lines of both these forms. H. H.

Silica. I. Loss of Water of Kaolin and its Behaviour in the Solid State towards the Carbonates and the Oxides of the Alkaline Earths. G. TAMMANN and W. PAPE (*Z. anorg. Chem.*, 1923, **127**, 43—67).—Experiments were carried out with carefully washed Oschatz earth dried at 150°, and its dehydration and the behaviour of the carbonates and the oxides of the alkaline earths towards the anhydrous compound Al_2O_3,SiO_2 formed and towards kaolin were studied. At 550°, kaolin loses water and decomposes into alumina and silica, and at 930° the alumina undergoes a change. These conclusions are based on the following results. After heating at 550°, the alumina of kaolin is soluble in acids, further heating at 900° renders pure alumina and that of kaolin difficultly soluble in acids. Pure alumina evolves heat at 850—1060°; kaolin evolves heat at 930°, the amount being proportional to its alumina content. Both alumina and kaolin show an increase in density at still higher temperatures, and they both lower the dissociation temperature of the alkaline-earth carbonates (1 atmosphere by about 220°). W. T.

Crystal Structure of Potassium Hydrogen Fluoride. RICHARD M. BOZORTH (*J. Amer. Chem. Soc.*, 1923, **45**, 2128—2132).—The positions of the potassium and fluorine atoms in tetragonal potassium hydrogen fluoride have been determined by *X*-ray photographs. The dimensions of the unit cell are 5·67 × 5·67 × 6·81 Å. The structure may be described as an ammonium chloride arrangement of potassium atoms and fluorine "dumb-bells," the two atoms of each "dumb-bell" lying in a plane perpendicular to the tetragonal axis. For the hydrogen atoms, there are two possible positions, one of which is in the middle of the "dumb-bell," forming an HF_2'-ion. The distance between potassium and fluorine atoms is 2·77 Å., between two potassium atoms 3·41 and 4·01 Å., and between two fluorine atoms 2·25 Å. In the case of potassium fluoride, the distance between potassium and fluorine is 2·68 Å. and between two potassium atoms 3·79 Å. The complete unit cell contains 4 mols. of potassium hydrogen fluoride. J. F. S.

Saturated Solutions of Potassium and Magnesium Sulphate. S. M. LEVI (*Z. physikal. Chem.*, 1923, **106**, 93—104).—Solubility determinations of the system magnesium sulphate-

potassium magnesium sulphate have been made at a series of temperatures from 0° to 37·8°, and a further series for the system potassium sulphate–potassium magnesium sulphate for temperatures between 0° and 63·4°. The values interpolated for 25° from the present measurements agree with those determined by van Klooster (A., 1917, ii, 471). The solubility curve of magnesium sulphate for the system potassium sulphate–double salt shows a sharp break at about 52°, which is not in agreement with the dilatometric and tensimetric determinations of the transition point of the system potassium sulphate–schönite–leonite determined by van't Hoff as 47·5°. A simple process is described whereby thermometrically the transition points of the systems double salt–ice–less soluble component, and double salt–both components, may be distinguished from one another. J. F. S.

The Energy Content and Constitution of the Potassium Polythionates. F. MARTIN and L. METZ (*Z. anorg. Chem.*, 1923, **127**, 83—100).—The heats of formation of potassium di-, tri-, tetra-, and penta-thionate, potassium sulphite, and potassium thiosulphate were determined in a Berthelot-Mahler bomb; to ensure complete combustion it was necessary to mix the salt with potassium chlorate and magnesium. The heats of formation were found to be $K_2S_2O_6$, 415 Cal.; $K_2S_3O_6$, 401 Cal.; $K_2S_4O_6$, 393 Cal.; $K_2S_5O_6$, 386 Cal.: K_2SO_3, 273 Cal., and $K_2S_2O_3$, 283 Cal. Thus the addition of solid sulphur to the polythionates is endothermic. The constitution of these salts is discussed from the point of view of Werner's co-ordination theory. They are given a binuclear structure—the central atom sulphur being assigned a co-ordination number equal to 4 and a valency of +6, whilst the co-ordinated sulphur atoms have a valency of −2. Pentathionic acid is formulated thus:

$$H\left[\begin{array}{cc}O & O\\ & S\\ O & S\end{array}\right]S\left[\begin{array}{cc}O & O\\ & S\\ S & O\end{array}\right]H$$

The method of preparation of the salts is given in detail. W. T.

Mechanism of certain Catalysed Reactions. CARLO SANDONNINI (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 84—88).—Investigation of the changes occurring in solutions of potassium and ammonium hydrogen sulphites in presence of selenium indicates that, under certain conditions, the total reaction may be expressed by the equation: $4MHSO_3 \longrightarrow 2M_2SO_4+SO_2+S+2H_2O$. This probably takes place in the three stages, (1) $M_2SO_3+Se \longrightarrow M_2SSeO_3$, (2) $M_2SSeO_3+M_2SO_3+2H_2SO_3 \longrightarrow M_2SO_4+M_2S_3O_6+Se+H_2O$, and (3) $M_2S_3O_6 \longrightarrow M_2SO_4+SO_2+S$. Thus, the true catalytic action of the selenium would cease when only one-half of the total sulphuric acid is formed. It is found that, when reprecipitation of the selenium occurs in accordance with equation (2), the quantity of sulphuric acid present does not correspond exactly with one-half of the final amount, and that the latter exceeds what should be formed according to equations (1) and (2). These divergences

may be attributable to the facts that the end of the initial phase cannot be gauged exactly, that the reactions become superposed, and that the excess of sulphur dioxide undergoes partial oxidation. The quantity of sulphur which separates and that of sulphur dioxide not participating in the reaction do not, indeed, correspond exactly with those calculable from the above reactions. It is possible also that secondary reactions lead to the formation first of selenothionate and thiosulphate and afterwards of other polythionates, and that the formation and subsequent decomposition of these compounds give rise to the divergences mentioned above.

T. H. P.

Solubility of Sodium Chlorate. HUGH CHESTER BELL (T., 1923, **123**, 2713—2714).

Stability of Solutions of Alkali Chlorites. G. R. LEVI and G. NATTA (*Gazzetta*, 1923, **53**, 532—538; cf. this vol., ii, 767).—Solutions of chlorites are not altered at 100°, even when hydrogen or oxygen is passed through them. Various finely divided metals are, however, capable at even moderately high temperatures of exerting a marked catalytic effect on the decomposition of chlorites which, in presence of palladium or gold, is expressed by the equation $9NaClO_2=4NaCl+5NaClO_3+O$ (1); this reaction is modified by a current of hydrogen to $2NaClO_2=NaCl+NaClO_3+O$ (2). Similar decompositions are produced by platinum and nickel, but in these cases the loss of oxygen is greater, although the decomposition is less rapid; the effect of copper is negligible. Decomposition of solutions of chlorites in quartz vessels exposed to sunlight is accompanied by formation of ozone, which probably results also from reaction (1).

The decomposition of chlorite into chloride and chlorate by the agency of catalysts corresponds only partly with that effected when the solid salt is heated at 180—200°, the loss of oxygen in the latter case being very small (A., 1922, ii, 567). T. H. P.

Stability of Sodium Thiosulphate Solutions. MARTIN KILPATRICK, jun., and MARY L. KILPATRICK (*J. Amer. Chem. Soc.*, 1923, **45**, 2132—2135).—The stability of several $0.01N$-solutions of sodium thiosulphate has been investigated over a period of eight months. It is found that freshly boiled redistilled water yields a solution of thiosulphate that is more stable than a solution made with ordinary laboratory distilled water, ordinary distilled water, or redistilled water through which carbon dioxide-free air has been bubbled. Carbon dioxide, oxygen, and dilute sodium hydroxide have very little effect on the stability of solutions of sodium thiosulphate. The decomposition in these solutions is caused by bacteria. J. F. S.

The Ammines of the Alkali Halides. WILHELM BILTZ and WERNER HANSEN (*Z. anorg. Chem.*, 1923, **127**, 1—33).—The following compounds were prepared and investigated; the heats of formation in calories and the temperature at which the dissociation pressure equals 100 mm. of mercury are given. $LiCl,NH_3$, 12·4,

+70°; $LiCl,2NH_3$, 11·5, +44°; $LiCl,3NH_3$, 10·7, +23·5°; $LiCl,4NH_3$, 8·8, −20·5°; $LiCl,5NH_3$, 8·0, −44°; $LiBr,NH_3$, 13·6, +102°; $LiBr,2NH_3$, 11·7, +48°; $LiBr,3NH_3$, 11·1, +33°; $LiBr,4NH_3$, 10·2, +20°; $LiBr,5NH_3$, 8·05, −44°; $LiBr,6{\cdot}5NH_3$, 6·9, −67°; LiI,NH_3, 16·0, +169°; $LiI,2NH_3$, 13·8, +108°; $LiI,3NH_3$, 12·2, +64°; $LiI,4NH_3$, 11·6, +60·5°; $LiI,5NH_3$, 8·1, −43°; $LiI,5{\cdot}5NH_3$, 7·2, −62°; $LiI,7NH_3$, 7·1, −65°; $NaCl,5NH_3$, 7·8, −49°; $NaBr,5{\cdot}25NH_3$, 8·45, −31·5; $NaBr,5{\cdot}75NH_3$, 6·95, −66°; $NaI,4{\cdot}5NH_3$, 9·4, −3°; $NaI,6NH_3$, 7·5, −52°; $KBr,4NH_3$, 7·15, −64°; $KI,4NH_3$, 7·65, −46°; $KI,6NH_3$, 7·35, −55°; $RbBr,3NH_3$, 7·1, −62°; $RbI,6NH_3$, 7·5, −55°. The compound $NaCl,2{\cdot}5NH_3$ described by Friedrich (A., 1921, ii, 503), could not be isolated. The capacity of the alkali halides to co-ordinate ammonia increases from cæsium to lithium and from chlorides to iodides. Methods of investigation were as previously described (A., 1922, ii, 59). W. T.

The System Ammonium Nitrate–Ammonia. F. HALLA and K. HIRSCHKO (*Z. anorg. Chem.*, 1923, **127**, 137—152).—Diver's liquid, which is formed by passing ammonia over ammonium nitrate, is only stable up to a temperature of 23·7° with a pressure of 1 atmosphere of ammonia. Above this temperature it exists in a metastable condition (supersaturated solution). The system ammonia–ammonium nitrate forms a simple binary system. The rate of absorption of allotropic forms of the nitrate were found to be the same. W. T.

Double Decomposition in the Absence of Solvents. IV. The Systems Formed by Metallic Nitrates, Chlorates, and Halides. A. G. BERGMANN (*J. Russ. Phys. Chem. Soc.*, 1923, 474—492).—A number of binary mixtures of salts have been investigated by the thermal method.

A.—Systems with silver nitrate. The system $AgNO_3$–$HgBr_2$ is complex in nature, the liquidus curve showing a maximum in the region of 50%, but this is probably not due to compound formation, as the molten mass solidifies over a large range of temperature. The mixtures after melting are hygroscopic; they are very sensitive to overheating. The system $AgNO_3$–$HgCl_2$ is similar in nature; the liquidus curve also shows a break in the region of 50%, but the mass solidifies even more slowly; the mixtures are also hygroscopic. The system $AgNO_3$-CdI_2 was only partly studied, because mixtures containing more than 20% of the latter constituent readily underwent decomposition. The eutectic is observed in the neighbourhood of 93° and 11% CdI_2, the liquidus curve is very steep, doubtless owing to the formation of complex compounds, but no double decomposition occurs; the crystals separating when the melt solidifies are not like the hexagonal plates of cadmium iodide. A very similar result is obtained with cadmium chloride; the liquidus curves are also very steep. Silver chloride and iodide appear to be quite insoluble in cadmium nitrate, either in the molten state or in solution.

On melting silver nitrate with thallium chloride or iodide double

decomposition is complete, the two immiscible layers obtained consisting of silver halide and thallium nitrate; thallium thus behaves in the same way as the alkali metals. The calculated thermal effect is −11·2 and −13·57 cal., respectively, and therefore favourable to the reaction.

B.—Nitrates of alkalis and alkaline earths. The nitrates of the alkalis and the alkaline-earth group are all partly miscible with mercuric halides in the molten state; here, again, the greater the miscibility the less is the negative thermal effect of the double decomposition.

C.—Chlorates. The chlorates of sodium, potassium, and silver form two layers when melted with mercuric chloride or iodide, but they were not studied in detail; the thermal effect of double decomposition is actually positive.

The various liquidus curves for systems containing silver nitrate are tabulated; the flattest curves represent systems where double decomposition takes place, whilst the steepest denote the formation of complexes; the curves of systems containing chlorides are the flattest, those with iodides the steepest. G. A. R. K.

Changes between Metals or Metallic Oxides and Carbon. KURT NISCHK (*Z. Elektrochem.*, 1923, **29**, 373—390).—A graphical method of representation is described by means of which equilibria in ternary and quaternary systems may be plotted. A number of metals have been investigated with regard to their affinity for carbon in comparison with their affinity for oxygen by melting a mixture of the oxide and carbon together. It is shown that when copper is added to the mixture a definite percentage of the metal from the oxide is found alloyed with the copper; the percentage depends on the affinity of the metal for carbon. Barium and strontium on reduction of the oxide passed completely into carbide even in the presence of metallic copper. In the case of calcium and magnesium, a small amount of these metals was found in the copper. Glucinum and aluminium can exist to the extent of several per cent., alloyed with copper, in the presence of carbon. Boron, silicon, and titanium show a still greater affinity for carbon. Chromium, molybdenum, and manganese exhibit a great affinity for carbon, but they can exist alloyed with copper in the presence of carbon. The tendency to carbide formation decreases with the change in the position of the element in the periodic system, from group I to group VIII and in the case of cobalt and nickel it is a minimum. Microscopic investigation in the case of chromium and molybdenum shows that the carbides richest in metal are Cr_2C and Mo_2C, respectively. Some experiments were made with calcium carbide as reducing agent; this substance is very useful, since with a suitable addition of fluorspar a completely molten mixture is obtained. A method is described whereby glucinum, boron, silicon, and titanium can be cheaply alloyed with copper. Photomicrographs of sections of the reaction mixtures and copper alloys are included in the paper. J. F. S.

Calcium Carbonate Hexahydrate. JOHN EDWIN MACKENZIE (T., 1923, **123**, 2409—2417).

The Solubility and Hydrolysis of Calcium Carbonate. H. O. ASKEW (*Trans. New Zealand Inst.*, 1923, **54**, 791—796).—The solubility of calcite in gas-free water at 25° in a closed vessel is $13 \cdot 4 \times 10^{-5}$ g.-mols. per litre. The presence of traces of carbon dioxide exerts a considerable influence on the solubility, the mean value found when using ordinary distilled water being $19 \cdot 6 \times 10^{-5}$ g.-mols. per litre. The solubility is affected, apparently in an irregular manner, by the presence of other salts. In the measurement of hydrolysis, the velocity-constant method was not successful and some unknown factor seemed to affect electromotive force measurements, so that trustworthy values were not obtained.

H. J. E.

The Dissociation of Dolomite. CECIL S. GARNETT (*Min. Mag.*, 1923, **20**, 54—59).—The statement that dolomite [$CaMg(CO_3)_2$] when heated first breaks down with magnesium oxide and calcium carbonate ($MgO+CaCO_3$) is not confirmed. White, crystalline dolomite-rock from Steetley near Worksop (which gave on analysis CaO 30·4, MgO 21·4, CO_2 47·6, SiO_2 0·16, Al_2O_3 0·09, FeO 0·41%) was heated in a flask through which passed a current of air, and the carbon dioxide evolved was absorbed in potassium hydroxide solution. A selection of the observed values is:

Temp.	350°	550°	650°	760°	805°	830°	898°
CO_2%	0·01	0·42	2·21	19·6	33·1	44·8	47·6

The presence of free calcium oxide was established after dissociation had only commenced. The rock fragments suffered no contraction in volume by the heating. Grecian magnesite ($MgCO_3$) heated under the same conditions lost 0·84% CO_2 at 500°; dissociation was vigorous from 540° and complete below 650°. Artificially prepared magnesium carbonate ("magnesia alba") lost 0·72% CO_2 at 250°; dissociation was appreciable at 300° and complete at about 430°. L. J. S.

The Conversion of Calcium Phosphates into Chloro-derivatives of Phosphorus by Means of Sulphur Chloride. P. P. BUDNIKOV and E. A. SHILOV (*J. Soc. Chem. Ind.*, 1923, **42**, 378T).—Calcium phosphates may be converted almost quantitatively into phosphorus trichloride by heating them at 1,000° with sulphur chloride and a catalyst. Suitable catalysts are silica or coal, separately or together. It is advisable to convert calcium orthophosphate into the metaphosphate before heating with sulphur chloride. H. H.

Allotropy of Zinc. L. LOSANA (*Gazzetta*, 1923, **53**, 539—545).—Measurements of the variation with temperature of the cubical expansion of zinc indicate the existence at 176° and 320° of singular points which indicate with certainty the occurrence of allotropic transformations. When the temperature variations are measured, in comparison with those of a substance exhibiting no allotropic changes, by means of highly sensitive thermo-electric couples, small but distinct divergences are observed at 173° and 323°. The mean values found for these transformation points are 174° and

322° for the α- to β- and β- to γ-changes, respectively. If the zinc contains traces of iron or tin, the former of these points is not observed, whereas when cadmium is present the distance between the two points is considerably diminished. Between −150° and the ordinary temperature, no anomaly occurs except a change in the direction of the thermal curve at about −80° which is too slight to justify the assumption of an allotropic transformation. T. H. P.

Use of Mercury in the Purification of Zinc Sulphate Solutions. SAMUEL FIELD and WILLIAM E. HARRIS (*Trans. Amer. Electrochem. Soc.* [advance copy], 1923, 269—293).—The need for zinc sulphate solutions of a high degree of purity in the electrolytic zinc industry is explained and the advantages of a pure salt are pointed out. The use of mercury as a purification agent is based on the overvoltage of mercury against hydrogen; this is discussed in detail. By amalgamating finely divided negative metals, such as zinc and aluminium, complete purification can be readily and economically effected even in strongly acid solutions. The mercury is added to the zinc liquors as mercuric sulphate, followed by zinc powder or zinc blue. The impurities are eliminated in preference to the hydrogen of the acid added. Economy of zinc is thus effected, and the method becomes applicable also for cases in which high acid content would prohibit purification owing to high consumption of zinc. J. F. S.

Attempted Separation of the Isotopes of Lead. The Atomic Weight of Lead. O. HÖNIGSCHMID and M. STEINHEIL (*Ber.*, 1923, **56**, [*B*], 1831—1837).—Lead chloride was fractionally distilled in a high vacuum by Brönstedt and von Hevesy, and the end fractions were submitted to the authors for atomic-weight determinations. The samples were fused and distilled in quartz apparatus in a current of hydrogen chloride before analysis, which was carried out nephelometrically against pure silver dissolved in nitric acid in order to determine the ratios $PbCl_2 : 2Ag$ and $PbCl_2 : 2AgCl$. The result for the more volatile fraction (mean of ten) was $Pb = 207{\cdot}229 \pm 0{\cdot}003$, and for the less volatile fraction (mean of ten) $Pb = 207{\cdot}236 \pm 0{\cdot}003$. This difference is too small, in the authors' opinion, to warrant any claim for separation, and they suggest the value $Pb = 207{\cdot}23$ for ordinary lead. H. H.

Atomic Weight of Uranium-lead. O. HÖNIGSCHMID and L. BIRCKENBACH (*Ber.*, 1923, **56**, [*B*], 1837—1839; cf. preceding abstract).—The atomic weight of lead from Upper Katanga in the Belgian Congo was determined by the method described in the preceding abstract. The mean of three determinations gave $Pb = 206{\cdot}048$, whence the authors conclude this to be pure uranium-lead. H. H.

Double Decomposition in the Absence of Solvents. III. The Systems Thallium Nitrate : Mercuric Chloride and Bromide. A. G. BERGMANN, T. A. HENKE, and F. M. ISAÏKIN (*J. Russ. Phys. Chem. Soc.*, 1923, **54**, 466—473; cf. this vol., ii, 568).—In continuation of previous work, the above systems have

now been examined and the results were found to confirm the theoretical conclusions already expressed; no double decomposition is observed. Thallium nitrate forms an equimolecular compound with mercuric bromide, melting at 152°; there is, in addition, an eutectic at 146° and 30% of mercuric bromide; the cooling curves are, otherwise, of simple type. With mercuric chloride (m. p. 282°, rhombic), thallium nitrate forms two compounds,

$$TlNO_3,HgCl_2,$$

and $2TlNO_3,HgCl_2$. The transition points observed in this system are the eutectic of the latter compound and thallium nitrate, corresponding with 12·8% of mercuric chloride and 176°; the melting point of the compound $2TlNO_3,HgCl_2$ at 195°; another eutectic at 192° and 37% of mercuric chloride; the melting point of the equimolecular compound at 202·5° and the eutectic formed by this compound and mercuric chloride at 197°. No solid solutions appear to be formed. The equimolecular compound crystallises not unlike thallium nitrate, but the crystals are better defined, whilst the compound $2TlNO_3,HgCl_2$ forms distinctive long needles.

G. A. R. K.

Reduction of Copper Oxide by Carbon Monoxide and the Catalytic Oxidation of Carbon Monoxide in the Presence of Copper and Copper Oxide. HOWARD ALGERNON JONES and HUGH STOTT TAYLOR (*J. Physical Chem.*, 1923, **27**, 623—651).—The reduction of copper oxide by carbon monoxide has been investigated under varying conditions. It is shown that the process is autocatalytic, copper being the auto-catalyst, the reduction occurring at the copper-copper oxide interface. The retarding effects of carbon dioxide and oxygen on the primary reaction of the reduction process, that is, the formation of copper nuclei, are pointed out. The mechanism for the combination of carbon monoxide-oxygen mixtures over copper oxide is shown to be alternate reduction and oxidation of the copper oxide. The mechanism for the combination of carbon monoxide-oxygen mixtures over copper is shown to be the oxidation of an adsorbed layer of carbon monoxide. It is shown that oxygen is a "permanent poison" in the combination of carbon monoxide with oxygen over copper.

J. F. S.

Cupric Oxide Jellies. HARRY B. WEISER (*J. Physical Chem.*, 1923, **27**, 685—691).—Hydrated cupric oxide jellies are formed when a suitable concentration of colloidal oxide is precipitated at a suitable rate. The desired conditions may be realised by adding ammonia to cupric acetate in the presence of a small amount of sulphate and allowing the colloidal solution to precipitate spontaneously. Jellies are not formed by adding ammonia to cupric acetate alone, since a colloid of suitable concentration cannot be prepared in this way.

J. F. S.

Baskerville and Catlett's Lanthanates. FERRUCCIO ZAMBONINI and GUIDO CAROBBI (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 53—59).—In criticising the work of Baskerville and Catlett

(A., 1904, ii, 260), the authors point out that the resemblance between lanthanum and aluminium is slight and quite insufficient to suggest the existence of lanthanum compounds corresponding with the aluminates; unlike aluminium, which is markedly amphoteric, lanthanum shows very distinct basic properties. The supposed compound, $Na_2La_4O_7$, is shown to be a mixture of lanthanum oxide, various indefinite substances, and the double carbonate, $La_2(CO_3)_3,Na_2CO_3,12H_2O$, the last being formed by the action of water on the product obtained when lanthanum oxide is fused with sodium carbonate. The other compounds obtained by Baskerville and Catlett by heating lanthanum oxide with metallic hydroxides on a water-bath, namely, $NaH_9La_5O_{15},4H_2O$, $LiH_9La_5O_{15},2H_2O$, $KH_9La_{10}O_{15},15H_2O$, and $Ba(H_9La_5O_{15})_2$, are composed of lanthanum oxide and hydroxide, together with the hydroxide and carbonate of the alkali or alkaline-earth metal; the first two of these compounds may contain also lanthanum carbonate, and double carbonates likewise may be present, although the protracted digestion on the water-bath would probably completely destroy them. T. H. P.

Ternary Alloys of Aluminium, Zinc, and Tin. L. LOSANA and E. CAROZZI (*Gazzetta*, 1923, **53**, 546—554).—This work was completed before the publication of that of Crepaz (this vol., ii, 641).

The metals employed contained, respectively, 99·83% of aluminium, 99·92% of zinc, and 99·92% of tin. For the system aluminium–tin, a few melting-point estimations were made in the region between 0 and 10% of aluminium, the results obtained differing only slightly from those of Heycock and Neville (T., 1890, **57**, 376) and of Gwyer (A., 1906, ii, 544). Similarly for the system aluminium–zinc, the few values found agree well with Rosenhain and Archbutt's complete investigation (A., 1911, ii, 895).

In the ternary system, the eutectic contains 1·46% of aluminium, 10·37% of zinc, and 88·17% of tin, melts at 194°, and is characterised clearly by the maximum time of crystallisation with respect to the other alloys. Aluminium and zinc form solid solutions over a moderately wide region of the diagram, the mixed crystals exhibiting distinct transformations at temperatures varying with the proportion of aluminium present; the same happens when a little tin is present. Alloys containing high percentages of zinc show a transformation point corresponding with the passage from the third to the second form of this metal, but the thermal change is very slight and difficult to detect. Of greater magnitude, although not very distinct, is the variation due to the change from the third to the second modification of the tin. In no case is the point of transformation of β- to α-zinc detectable. T. H. P.

An Example of Polymorphism in an Intermetallic Compound. DAVID STOCKDALE (*Trans. Faraday Soc.*, 1923, **19**, 135—139).—Evidence is given, from an examination of the equilibrium curves and of the microstructure of aluminium–copper alloys, for the existence of the compound Cu_2Al containing 17·5% Al and melting at 1016°, but unstable above 1015°. On cooling

alloys containing 14 to 21% of aluminium an arrest point occurs between 875° and 770° and is at the maximum in the alloy containing 17·8% of aluminium, corresponding with Cu_2Al. Addition of copper lowers this point considerably, and addition of aluminium slightly. No micrographical change takes place on cooling through the arrest point; it is therefore probable that the heat evolution or absorption is due to a change in the arrangement of the atoms or molecules in the compound Cu_2Al itself, *i.e.*, to a polymorphic transformation [cf. *J.S.C.I.*, 1923, 556A]. A. R. P.

Iron Carbide. Franz Wever (*Mitt. Kaiser Wilh.-Inst. Eisenforsch.*, 1922, **4**, 67—80; from *Chem. Zentr.*, 1923, iii, 187).—By *X*-ray analysis it is shown that the forms of cementite shown in the iron–carbon thermal diagram are not distinguishable by their lattice structure. Iron carbide, Fe_3C, crystallises in a rhombic lattice denoted by the quadratic form $\sin^2\theta/2=0{\cdot}0464x^2+0{\cdot}0367y^2+0{\cdot}0208z^2$. The edge lengths are $a=4{\cdot}481$ Å., $b=5{\cdot}034$ Å.; $c=6{\cdot}708$ Å. The density is calculated therefrom as 7·82. Data by the Debye-Scherrer method above 210° show that the magnetic transformation is not associated with a change in the type of lattice. The quadratic form is expressed by $\sin^2\theta/2=0{\cdot}0456x^2+0{\cdot}0362y^2+0{\cdot}0203z^2$. The edge lengths are $a=4{\cdot}52$ Å.; $b=5{\cdot}08$ Å.; $c=6{\cdot}77$ Å. G. W. R.

The Acid Decomposition of Metallographically Defined Iron and Manganese Carbide Alloys. R. Schenck, J. Giesen, and Fr. Walter (*Z. anorg. Chem.*, 1923, **127**, 101—122).—The alloys (iron–carbon and iron–manganese–carbon) were dissolved in hydrochloric acid, and the hydrocarbons evolved identified by (1) bromination, (2) condensation by liquid air, and (3) absorption by charcoal. In the case of the iron–carbon alloys and those of low manganese content, the chief gaseous products are propylene, Δ^β-butylene, ethylene, the higher olefines, methane, and ethane. In the case of the iron-manganese carbon alloys rich in manganese, the chief product is octene; some still higher olefines were also found, but ethane and ethylene could not be detected. Quantitative results are given. W. T.

Chlorites of certain Cobaltammines. G. R. Levi (*Atti R. Accad. Lincei*, 1923, [v], **32**, i, 623—626).—*Hexamminecobalt chlorite*, $[Co(NH_3)_6](ClO_3)_2,H_2O$, prepared from the luteo-chlorite and silver chlorite, forms slender, orange-yellow needles, explodes on percussion and, when treated in solution with cupric chloride, yields the double salt, $[Co(NH_3)_6]Cl_3,CuCl_2$.

Chloropentamminecobalt chlorite, $[Co(NH_3)_5Cl](ClO_2)_2$, obtained similarly, gradually emits chlorous vapours, and is exploded when struck, but gives no double compound with cupric chloride. Aquopentamminecobalt chlorite, obtainable in solution, cannot be isolated in the solid form.

A table is given showing all the chlorites, numbering 34, now known. According to the results as yet obtained, there exists but little analogy between chlorites and nitrites.

The solubilities of barium, lead, and silver chlorites have been measured. At 0°, 100 g. of solution contain 30·5, 0·035, and 0·17 g. respectively, and at 100°, 44·7, 0·41, and 2·11 g., respectively, of these salts. T. H. P.

Nickel Sulphide. FRITZ EPHRAIM (*Ber.*, 1923, **56**, [*B*], 1885—1886; cf. this vol., ii, 423).—Nickel sulphide is readily soluble in yellow ammonium polysulphide solution, but much less soluble in colourless ammonium sulphide. By analogy with copper sulphide, of which the same is true, which forms the red ammonium copper tetrasulphide, it was thought that a similar compound might exist in the case of nickel. Nickel sulphate was added to a solution of ammonium polysulphides in an air-tight flask, and after some days a considerable quantity of a black, crystalline substance of composition intermediate between $(NH_4)NiS_4$ and $(NH_4)NiS_5$ was deposited. Salts of cobalt, iron, zinc, manganese, and cadmium did not give similar compounds. H. H.

Density Measurements of some Simple and Complex Salts of Nickel and Cobalt. WILHELM BILTZ and ERWIN BIRK (*Z. anorg. Chem.*, 1923, **127**, 34—42).—The lattice structure of hexamminenickelous chloride has been measured by Scherrer (A., 1922, ii, 514); the lattice constants of the hexammines of the nickel group can be calculated from their densities, assuming that their structures are the same. The following values for the densities were obtained, high boiling fractions of petroleum (d=0·7975—0·7998) being used as the pyknometer liquid. $NiCl_2$ sublimed 3·521, $NiCl_2$ (prepared from the hexammine) 3·508. $NiBr_2$ sublimed 5·098, $BiBr_2$ (prepared from the hexammine) 5·042. NiI_2 (prepared from the hexammine) 5·834. $CoCl_2$ 3·367. $CoBr_2$ 4·849. CoI_2 5·584. $[Ni(NH_3)_6]Cl_2$ 1·468. $[Ni(NH_3)_6]Br_2$ 1·889. $[Ni(NH_3)_6]I_2$ 2·113. $[Co(NH_3)_6]Cl_2$ 1·479. $[Co(NH_3)_6]Br_2$ (prepared by the wet method) 1·871, (prepared by the dry method) 1·879. $[Co(NH_3)_6]I_2$ 2·096. $[Co(NH_2)_6]Cl_3$ 1·710. $[Co(NH_3)_6]Br_3$ 2·340. $[Co(NH_3)_6]I_3$ 2·746. Agreements with previous determinations are not good. The method of preparation of the salts is given in detail. W. T.

The Lattice Structure, Directions of Slip, and Slip Planes of White Tin. H. MARK and M. POLANYI (*Z. Physik*, 1923, **18**, 75—96).—The authors find that the phenomena associated with the extension of a single crystal of tin are analogous to those exhibited under similar conditions, by a single crystal of zinc (*ibid.*, 1922, **12**, 58). White tin crystallises in the ditetragonal-bipyramidal system, space group D_{4h}^{19}. The lengths of the axes of the crystal structure are respectively a 5·84 Å., c 3·15 Å., and the elementary cell contains four atoms. Slipping occurred in the directions [100], [101], and [111]. Of these directions, [100] occurred most frequently, and [111] only at a high temperature. The slip planes were represented by (110) and (100), the former occurring more frequently (8 : 3) than the latter. J. S. G. T.

Preparation of Coarsely Crystalline, Anhydrous Titanium Trichloride, and the Mechanism of the Reduction of Titanium Tetrachloride by Means of Hydrogen. FRIEDRICH MEYER, ALFRED BAUER, and RICHARD SCHMIDT (*Ber.*, 1923, **56**, [*B*], 1908—1914; cf. A., 1912, ii, 1051).—The two requirements for the successful preparation of coarsely crystalline titanium trichloride by reduction of the tetrachloride are, first, a steep temperature gradient to ensure rapid cooling, and secondly, the depression of the hydrogen chloride concentration. The first condition is best secured by using a non-conducting (quartz) tube of narrow bore, with air cooling at the receiver end. The second is attained most easily by the addition of metallic titanium to the reaction mixture. It is shown that the reduction is not direct, but that three reactions, $TiCl_4+H_2=TiCl_2+2HCl$; $TiCl_2+TiCl_4=2TiCl_3$; $2TiCl_3+2HCl=2TiCl_4+H_2$, may proceed simultaneously. H. H.

The Chemistry of Hafnium. G. VON HEVESY (*Chemistry and Industry*, 1923, **42**, 929—930).—The natural oxides of zirconium, such as baddeleyite, contain only 1% or 2% of the new element No. 72, hafnium, whilst the common zirconium minerals, such as zircon, contain up to 7%. The minerals richest in hafnium are the secondary zirconium minerals alvite, cyrtolith, naegeite, and malakon, which may yield zirconium containing up to 30% of hafnium. The hafnium content of a specimen or preparation is determined by comparing the intensity of *X*-ray lines due to hafnium with the intensity of the line due to a known quantity of the neighbouring element No. 73 (tantalum) added to the specimen. Separation of hafnium from zirconium is accomplished through the different solubilities of their corresponding salts and the different basicity of their oxides. Zirconium potassium fluoride has a solubility of 2·6% at 20°, hafnium potassium fluoride nearly 3·0%. Hafnium ammonium fluoride forms prismatic, pseudo-hexagonal crystals. Hafnium ammonium oxalate and hafnium ammonium sulphate are more soluble than the corresponding zirconium salts, whilst, of the oxychlorides, that of hafnium is the less soluble. Hafnium is more basic than zirconium, and consequently when the latter is precipitated as a basic salt hafnium accumulates in solution. Concentrated preparations of hafnium are purified from zirconium by dissolving the oxychloride in alcohol and adding ether, when the basic salt, $Zr_2O_3Cl_2,5H_2O$, is precipitated; this is less soluble than the corresponding hafnium compound. The properties of hafnium are in every way much closer to those of zirconium than to those of thorium. In several cases, the solubility of a hafnium compound is greater than that of the corresponding zirconium or thorium compound. E. H. R.

Germanium. VI. Metallic Germanium. Reduction of Germanium Oxide. Preparation of Fused Germanium. Physical and Chemical Properties. P. M. DENNIS, KATHARINA M. TRESSLER, and F. E. HANCE (*J. Amer. Chem. Soc.*, 1923, **45**, 2033—2047; cf. this vol., ii, 570).—Germanium dioxide may be dehydrated by heating at 950° for three hours; the product is not volatile at 1,250° and is not hygroscopic. Germanium dioxide may

be reduced to the metal by the alumino-thermic method, but the metal obtained constitutes a yield of only 61%, and there is a big loss of germanium dioxide by volatilisation. Small quantities of germanium dioxide (2 g.) may be reduced completely to the metal, in the form of a grey powder, by heating for two hours at 540° in a current of hydrogen, and there is no loss of material as hydride. But if larger quantities (10—14 g.) are employed, the yield is always below the theoretical quantity, and a black deposit shading off to brown and yellow appears in the colder parts of the tube. Coherent germanium is best prepared from the powder by fusion with sodium chloride at 980—1,000° for thirty minutes. In this way, about 96% of the powder is recovered as a single, lustrous button; the residue remains with the flux as sodium germanate. Fusion with sodium sulphate gave only a 73·8% yield, the residue of the germanium being present as sulphide, due to reduction of the sodium sulphate. Borax also proved to be an unsuitable flux. Metallic germanium which is quite free from oxide does not lose weight when heated in highly purified hydrogen to temperatures not exceeding 800°, but volatilisation of germanium does take place when hydrogen is passed over the molten metal. Pure germanium melts at 958·5°. Germanium expands on solidification and gives rise to protuberances on the buttons as it cools. It has d_{20}^{20} 5·35, which compares favourably with the value 5·36 calculated from *X*-ray analysis. Germanium is extremely brittle, and has a hardness between that of adularia and that of epidote, about 6·25. Germanium crystallises in elongated crystals bounded in some cases by octahedral faces and often covered with dendritic branches. Some of the crystals obtained were 3 cm. long. The thermo-electric power of germanium is a linear function of the temperature, and the electrical resistance is an exponential function of the form $\log R = \log A + \alpha T + Q/kT$, except over the range 100° to 600°, where an inversion takes place. More exact examination shows that germanium passes through a gradual molecular inversion with two or more modifications between 117° and 560°. When heated at 730° in oxygen, germanium is incompletely oxidised to a mixture of germanous oxide and germanium dioxide; at higher temperatures the lower oxide volatilises, so that it is impossible to oxidise germanium completely in oxygen. Germanium is not attacked by hydrogen sulphide at temperatures below 200°, and the action of the gas is comparatively slight until the hydrogen sulphide commences to dissociate. The reaction then becomes one between germanium and sulphur, with the formation of germanous sulphide. Sulphur dioxide acts on crystallised germanium at temperatures a little below 500°; the reaction becomes rapid between 510° and 530°, with the formation of the dioxide and disulphide of germanium. At the ordinary temperature and at 90°, germanium is not attacked by water, 50% sodium hydroxide solution, 1 : 1-hydrochloric acid, concentrated hydrochloric acid, or 1 : 1-sulphuric acid. It is slightly tarnished by 10% sodium hydroxide, both cold and warm. Dilute nitric acid oxidises it superficially to the dioxide, but the concentrated acid, beyond darkening the surface slightly, had no other action. Concentrated

sulphuric acid has no action at the ordinary temperature, and only a very slight action at 90°. Hydrofluoric acid, 19N, has only slight action, but 3% hydrogen peroxide slowly converts the metal into the dioxide and dissolves it. Metallic germanium dissolves rapidly in molten potassium hydroxide, sodium hydroxide, sodium carbonate, potassium nitrate, and sodium peroxide; it dissolves slowly in molten potassium hydrogen sulphate and potassium chlorate, and is not attacked by molten potassium cyanide. Attempts to prepare germanium carbide were without success.

J. F. S.

Hydrosol of Vanadium Pentoxide. A. Dumanski (*Kolloid Z.*, 1923, **23**, 147—159).—The methods of preparation and the properties of vanadium pentoxide hydrosol have been investigated. It is shown that the hydrosol as well as solutions of vanadium pentoxide yield the ions of hexavanadic acid. Electrical conductivity measurements indicate a gradual hydrolysis of the pentoxide hydrosols on dilution with water. This hydrolysis is confirmed by measurements on the absorption of light. The colloidal particles of vanadium pentoxide are negatively charged and are very small, so small as to be indistinguishable in the ultramicroscope. The sol is coagulated by electrolytes and the positive ion of the electrolyte is adsorbed. The adsorption compounds thus obtained pass, on keeping, into ordinary chemical compounds. Determinations of the depression of the freezing point indicate that the colloidal particles are not very large, and from these measurements the equivalent of the colloidal particle is deduced as approximately 1,000. The colloidal particles are given a formula of the type $[H_3V_6O_{17},(V_2O_5)_n]'$ or $[H_2V_6O_{17},(V_2O_5)_n]''$. Starting from the value of the equivalent as 1,000, the second of these formulæ in which $n=5$ is obtained, namely, $[H_2V_6O_{17},(V_2O_5)_5]''$. The double refraction of the sol increases with its age and with the formation of a turbidity in the sol. The gels of this colloid consist of orientated particles, which exhibit double refraction when they are still. Vanadium pentoxide sol on reduction furnishes the sols of lower oxides of vanadium. These sols are all charged negatively. J. F. S.

Atomic Weight of Antimony from Different Sources. I. Sheikh D. Muzaffar (*J. Amer. Chem. Soc.*, 1923, **45**, 2009—2013).—An account of preliminary determinations of the atomic weight of antimony obtained from stibnite from various sources. The experiments cover material obtained from Peru, Bolivia, Borneo, and Hungary. The antimony from all samples was purified by the same method and converted into the trichloride and the ratio between antimony trichloride and potassium bromate determined by titration. The reaction between the two substances is given by the equation $3SbCl_3+KBrO_3+6HCl=3SbCl_5+KBr+3H_2O$. The following results were obtained: Hungarian material, Sb=121·144 (7 expts.), Borneo material Sb=121·563 (7 expts.), Peruvian material, Sb=121·720 (7 expts.), and Bolivian material, Sb=122·374 (11 expts.). Each set of results is remarkably concordant. The author is of the opinion that the present results point

to the occurrence of a different distribution of the isotopes of antimony in the different stibnites. J. F. S.

The Hydrates of Antimony Pentoxide. GERHARDT JANDER and ARTHUR SIMON (*Z. anorg. Chem.*, 1923, **127**, 68—82).—Hydrates of antimony pentoxide were prepared by three methods, (1) the hydrolysis of the pentachloride at 0—1°, (2) hydrolysis at 100°, (3) oxidation of the trichloride by concentrated nitric acid and hydrolysis of the product at 60°. The products were dried on porous plates in the air, and were found to contain (1) 30·57, (2) 9·97, (3) 7·91 mols. of water to 1 mol. of the pentoxide. After drying over sulphuric acid, the water contents were (1) 3·68, (2) 2·17, (3) 0·60 mols. per mol. Sb_2O_5. Drying at 105° reduced the molecules of water per mol. of the pentoxide to (1) 2·43, (2) 1·02, (3) 0·45. The behaviour of the three hydrates towards alkali and phosphoric acid was investigated, and their vapour tension isotherms were measured. Results indicate that no definite hydrates were formed, but that gels were present, the behaviour of which depend on grain size, which varies with the method of preparation (cf. stannic acid, Mecklenburgh, A., 1914, ii, 529). Alcogels of the pentoxide were also prepared, and these were de-alcoholated by placing them over glycerol; the curves of de-alcoholation were similar to those of dehydration. The pentoxide was also able to take up benzene when kept in an atmosphere of the latter. W. T.

Bismuth Reduced by Dextrose. H. COUSIN (*J. Pharm. Chim.*, 1923, [vii], **28**, 179—181).—The black precipitate produced by the action of dextrose on a bismuth salt in presence of alkali was found on analysis to contain different amounts of bismuth, the percentage of the metal present increasing with the proportion of dextrose and sodium hydroxide used in the reaction. By adding a large excess of dextrose, the reaction may be utilised as a means of estimating bismuth, but the author does not recommend the method. H. J. E.

Electrical Conductivity and the Chemical Constitution of Alloys. II. The System Bismuth-Thallium. W. GUERTLER and A. SCHULZE (*Z. physikal. Chem.*, 1923, **106**, 1—17; cf. this vol., ii, 418).—The electrical conductivity of alloys of thallium and bismuth has been determined at 80° and 180°. The results confirm the condition diagram of this system obtained by other methods and make additions to the diagram. J. F. S.

Heterogeneous Equilibrium Produced by the Hydrolysis of Bismuth Chloride. KARL JELLINEK and WALTHER KÜHN (*Z. physikal. Chem.*, 1923, **105**, 337—355).—The equilibrium set up when various quantities of water are added to solutions of bismuth sesquioxide in hydrochloric acid has been examined by estimating the quantity of bismuth and hydrochloric acid left in solution after the addition of definite amounts of water. The solubility curve of the ternary system bismuth sesquioxide–hydrochloric acid–water has been determined, and it is shown that in certain concentrations the oxychloride, BiOCl, constitutes the solid phase, whilst in others

the hydroxide, $Bi(OH)_3$, is the solid phase. In alkaline solution, the oxychloride passes quantitatively into the hydroxide. The bismuth normal potential has been measured and the value +0·266 volt found in terms of the normal hydrogen electrode. The hydrogen-, chlorine-, and bismuth-ion concentrations have been determined for solutions of hydrochloric acid saturated with the oxychloride and by means of these results the law of mass action has been shown to be true for the reaction $Bi^{\cdot\cdot\cdot}+H_2O+Cl' \rightleftharpoons BiOCl+2H^{\cdot}$. The results make it probable that complex chlorobismuthic acids exist. Modified analytical methods have been deduced for the estimation of bismuth and chlorine in solutions of bismuth chloride. In the case of the estimation of bismuth the modification consists in precipitating as sulphide, filtering on a Gooch crucible, washing with acidified water, and drying at 110°. The free sulphur is then removed by placing the crucible in a furnace at 260—300° and heating for thirty minutes in a current of carbon dioxide. The results are accurate to 0·2%. J. F. S.

The Supposed Volatility of Tantalic Acid with Hydrofluoric Acid. Some Tantalum Compounds. OTTO HAHN and KARL F. PUETTER (*Z. anorg. Chem.*, 1923, **127**, 153—168). —Pure tantalic acid was prepared by the oxidation of the element in a stream of oxygen, and it was found to be non-volatile. Hydrofluoric acid solutions of pure tantalic acid on evaporation undergo hydrolysis; the residue shows no volatility on heating. Commercial tantalic acid loses weight on heating; this is due to the alkali which it contains. The higher the alkali content the greater is the volatility. The following new crystalline compounds were prepared: *tantalum hydrogen fluoride*, $HF,TaF_5,6H_2O$; *barium tantalum fluoride*, $3BaF_2,2TaF_5$; *monammonium tantalum fluoride*, NH_4F_2,TaF_5. Heating barium tantalum fluoride is a convenient method for the preparation of pure tantalum pentafluoride. W. T.

Platinum Oxide as a Catalyst in the Reduction of Organic Compounds. III. Preparation and Properties of the Oxide of Platinum obtained by the Fusion of Chloroplatinic Acid with Sodium Nitrate. ROGER ADAMS and R. L. SHRINER (*J. Amer. Chem. Soc.*, 1923, **45**, 2171—2179; cf. Voorhees and Adams, A., 1922, ii, 558; Carothers and Adams, this vol., ii, 310).—The fusion of sodium nitrate and chloroplatinic acid has been carried out at temperatures between 310° and 700°. The various samples of platinum oxide are tested as catalysts as follows. Maleic acid (20 g.) or benzaldehyde (20 g.) is dissolved in 150 c.c. of 95% alcohol. To the benzaldehyde solution, 1 c.c. of 0·0001*M*-ferrous chloride solution is added (Carothers and Adams, *loc. cit.*). The solutions are then reduced as previously described, using 0·25 g. of catalyst, and the time elapsing before reduction commences and the time taken for complete reduction are noted. The period of reduction is least when the catalyst has been prepared at about 500°, according to the benzaldehyde test, 400—500°, as shown by the reduction of maleic acid. The best temperature is certainly about 500°.

Analyses of the oxide agree with the formula PtO_2,H_2O. The

compound is amorphous; if produced at comparatively low temperatures, it is a very light brown, but this colour deepens as the fusion temperature is increased. The oxide dissolves only slightly in hot aqua regia, or in boiling, concentrated hydrochloric acid. It is insoluble in boiling, concentrated nitric acid. Nevertheless, boiling hydrobromic acid (10%), or cold hydrobromic acid of constant b. p., readily dissolves the oxide, with evolution of bromine, and formation of bromoplatinic acid. The oxide is rapidly dissolved when warmed with a mixture of hydrochloric and sulphurous acids. It causes the immediate decomposition of hydrogen peroxide, being itself apparently unchanged. It is gradually reduced when boiled with ethyl alcohol in the absence of air, acetaldehyde being produced.

It is shown that, for the production of the catalyst, the nitrates of lithium, potassium, calcium, barium, and strontium, are much less efficient than sodium nitrate. The oxide produced by this method is far more active as a catalyst than the other oxides of platinum described in the literature. Moreover, it is much more readily prepared. W. S. N.

A New Series of Complex Iridium Salts containing Hydrazine. L. Tschugaev (*Ber.*, 1923, **56**, [*B*], 2067—2068).—If potassium chloroiridiate be warmed in solution on the water-bath with excess of hydrazine hydrochloride, the solution assumes a reddish-brown colour and then contains the *complex acid*, $[Ir(N_2H_5)Cl_5]H$. The *platinitetrammine* salt,

$$[Ir(N_2H_5)Cl_5]_2[Pt(4NH_3)],$$

forms flesh-coloured platelets, and the *cæsium* salt, $[Ir(N_2H_5)Cl_5]Cs$, is also crystalline, and slightly more soluble in water than the former. The platinitetrammine salt is quantitatively converted into green Magnus's salt by treatment with excess of potassium chloroplatinite. H. H.

Mineralogical Chemistry.

New Lead-Copper Minerals from the Mendip Hills (Somerset). L. J. Spencer, with Analyses by E. D. Mountain (*Min. Mag.*, 1923, **20**, 67—92).—The only published analysis of Mendip minerals is that of mendipite by Berzelius (1823). A new analysis of this gave I, confirming the accepted formula $2PbO,PbCl_2$. Embedded in the mendipite from Higher Pitts, but in sparing amounts, are the two new minerals *chloroxiphite* (anal. II and III; $2PbO,PbCl_2,Cu[OH]_2$) and *diaboleite* (anal. IV;

$$Pb[OH]_2,PbCl_2,Cu[OH]_2).$$

Chloroxiphite, named from χλωρός, green, and ξίφος, a sword, is monoclinic (ac=62·75°) with a bladed habit and dull olive-green colour; the streak is a characteristic pale greenish-yellow; *H.* 2½. Parallel to *c* is a perfect cleavage and parallel to *a* a poorer cleavage. The pleochroism is strong (emerald-green and yellowish-brown); optically negative with axial plane perpendicular to the plane of

symmetry. The mineral is readily soluble in nitric acid. When heated it decrepitates, giving off water and lead chloride, and it melts to a brown liquid, which solidifies to a bright-green glass. All the water is lost below 250°. Diaboleite, named from διά, apart or distinct from boleite, is tetragonal ($a:c=1:0·95$), with bright sky-blue colour and pearly lustre on the basal cleavage. It is optically uniaxial and negative with marked pleochroism (dark-blue to almost colourless); n 1·98, $H.$ 2½. The mineral is soluble in nitric acid and behaves like chloroxiphite when heated.

By alteration, mendipite passes into hydrocerussite. This has hitherto been regarded as a rare mineral found only as films of minute pearly scales. The text-book formula is based on an analysis of the artificial crystalline material, which is identical with "white-lead" (*cerussa*). Large (5 cm.) rhombohedral crystals ($a:c=1:0·61$) from the Mendips have, however, been found in some old collections (*e.g.*, the Woodwardian collection, 1728, at Cambridge). There is a good cleavage with pearly lustre and snow-white colour parallel to the base, and the crystals are optically uniaxial and negative. When heated, the material decrepitates violently, breaking up into pearly scales and changing to orange yellow in colour. All the water is lost at 250°, and all the carbon dioxide on ignition (at 200° loss 0·87%, at 250° 2·76%). Analyses V and VI give the formula $2PbCO_3,Pb(OH)_2$. The presence of a little chlorine suggests an end-member $2PbCO_3,PbCl_2$ (distinct from phosgenite). By further alteration, hydrocerussite changes to cerussite ($PbCO_3$), and good pseudomorphs of cerussite after hydrocerussite have been found. Chloroxiphite alters to a mixture of hydrocerussite and malachite ($CuCO_3,Cu[OH]_2$), and in contact with the surrounding manganese-ore in which the nodules of lead-ore are embedded, has by further alteration given rise to crednerite ($CuMn_2O_4$ or CuO,Mn_2O_3).

Crednerite, hitherto regarded as a rare or doubtful mineral, has been found at Higher Pitts as radiating fan-like groups or hemispherical masses of thin plates with an iron-black colour and bright metallic lustre. It is perhaps monoclinic, but pseudo-hexagonal by twinning, and with perfect cleavages; opaque; streak, sooty black; $H.$ 4. It is not attacked by nitric acid, but dissolves in strong hydrochloric acid with evolution of chlorine (oxygen equivalent in anal. VII 6·22%). Deducting from anal. VII 6·10% of malachite and 1·05% of cerussite, seen in micro-sections to be intimately intermixed with the crednerite, the figures under VIII give the above formula.

	PbO.	CuO.	Mn_2O_3.	Cl.	CO_2.	H_2O.	Total less O for Cl.	Sp. gr.
I.	92·51	—	—	9·35	—	—	99·75	7·240
II.	81·15	10·90	—	7·19	—	2·56	100·18	6·763
III.	79·82	10·47	—	8·97	—	2·52	99·75	—
IV.	72·09	12·90	—	10·89	—	6·14	99·56	6·412
V.	86·52	—	—	0·27	11·21	2·23	100·17	6·80
VI.	86·43	—	—	0·32	11·32	2·00	100·00	6·786
VII.	0·88	36·57	60·62	—	1·88		99·95	4·972
VIII.	—	34·68	65·32	—	—	—	100·00	5·03

Other minerals described from Higher Pitts are wulfenite ($PbMoO_4$) and mimetite ($3Pb_3As_2O_8,PbCl_2$). The "green ore" mined in the Mendips centuries ago, apparently in some quantity, is shown from specimens preserved in the Woodwardian collection (1728) to be pyromorphite. L. J. S.

Crystallised Sulphates from Huelva, Spain. HENRY F. COLLINS (*Min. Mag.*, 1923, **20**, 32—38).—Pisanite resulting from the oxidation of cupriferous pyrites in the Rio Tinto mines gave analyses I—V, I—IV of well-developed monoclinic crystals and V of a stalagmitic mass, all agreeing with the formula

$$(Cu,Fe)SO_4,7H_2O.$$

Crystals with less than 7 or 9% CuO are light green, whilst those with more copper are blue in colour. Solutions containing more copper than the proportion 14% Cu to 8% Fe deposit chalcanthite together with the highly cupriferous pisanite. Chalcanthite is, however, less common than pisanite, owing to the usual excess of iron in the mine waters. Chalcanthite from the La Mimbrera mine near Zalamea gave VI.

In ancient (? Roman) workings in the Concepcion mine near Zalamea was found a cavity filled with mixed sulphates and fragments of partly sulphatised pyrites. Coquimbite as pinkish-violet crystalline masses, rarely as large, hexagonal prisms; anal. VII on material that had been dried over sulphuric acid, and the water consequently low for the formula $Fe_2(SO_4)_3,9H_2O$. Copiapite (VIII) as a friable aggregate of bright yellow, pearly scales. Voltaite (IX) as brilliant black or greenish-black octahedra, with $RO:R_2O_3:SO_3:H_2O=3·5:1:6·5:10$. Pink tufts of an undetermined mineral resembling halotrichite gave X, with $RO:R_2O_3:SO_3:H_2O=1:5:18:33$.

Roemerite (?) as white or yellowish silky tufts of acicular crystals on stalactites of pisanite from the Sotiel mine near Calañas gave XI, corresponding with $3(RO,SO_3)+R_2O_3,3SO_3+19H_2O$. Bloedite (?) as greenish, transparent crusts on old timbers in the abandoned Monte Romero mine gave XII. Goslarite as long, silky fibres hanging in bunches from the roof in the Almagrera mine at Tharsis gave XIII.

	Al_2O_3.	Fe_2O_3.	FeO.	CuO.	ZnO.	CaO.	MgO.	SO_3.	H_2O.	Insol.	Total.
I.	—	—	19·67	4·82	1·13	—	—	28·98	44·76	—	99·77*
II.	—	—	18·10	7·70	—	—	—	28·72	44·94	—	99·46
III.	—	—	15·40	10·58	—	—	—	28·82	44·52	—	99·32
IV.	—	—	15·08	11·51	0·35	—	—	28·66	44·70	—	100·30
V.	—	—	10·28	17·54	—	—	—	—	—	—	—
VI.	—	—	0·80	30·42	0·51	0·50	0·22	35·56	31·24	—	99·25
VII.	2·25	25·84	—	—	—	0·15	0·16	44·19	27·25	—	99·84
VIII.	†	30·65	0·72	—	—	0·50	0·50	47·97	18·72	0·10	99·16
IX.	2·14	11·38	14·47	0·22	—	0·90	3·00	47·02	16·44	—	99·22‡
X.	—	27·08	0·98	—	—	0·91	0·20	48·48	20·19	0·71	98·55
XI.	—	13·10	8·60	2·12	0·65	1·30	3·80	41·49	28·80	—	99·86
XII.	—	—	2·90	1·63	—	—	14·83	44·63	25·62	1·80	98·82§
XIII.	—	2·78	trace	0·96	24·78	0·30	0·55	28·12	41·32	—	99·47¶

* I, also MnO 0·31, NiO+CoO 0·10.

† VIII, a little Al_2O_3 included with Fe_2O_3.

‡ IX, also alkalis 3·65.

§ XII, also Na_2O 7·41.

¶ XIII, also NiO 0·66.

A large number of experiments are recorded on the crystallisation of mixed solutions of copper and ferrous sulphates in various proportions. In the monoclinic series of mixed crystals,

$$(Fe,Cu)SO_4,7H_2O$$

(pisanite), the maximum amount of copper that can be taken up is 14·65% Cu(=65·95% $CuSO_4,7H_2O$); and in the triclinic series, $(Cu,Fe)SO_4,5H_2O$ the maximum amount of iron is 0·84% Fe(=3·65% $FeSO_4,5H_2O$). L. J. S.

Scheelite of Traversella. G. Carobbi (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 79—83).—No complete analytical data for the scheelite of Traversella have yet been published. A brownish-yellow to honey-yellow crystal, carefully freed from impurities, gave on analysis:

H_2O.	WO_3.	MoO_3.	Nb_2O_5.	Ta_2O_5.	CaO.	BaO.	SrO.	MgO.
0·01	79·51	0·58	0·08	0·02	19·57	trace	trace	0·05

Yttria earths	Ce_2O_3.	La_2O_3,Nd_2O_3,Pr_4O_7.	Total.
0·06	0·03	0·05	99·96

T. H. P.

Oligoclase from North Carolina. Seitarô Tsuboi (*Min. Mag.*, 1923, **20**, 93—107).—A cleavage mass of oligoclase from Hawke mine, Bakersville, gave:

SiO_2.	Al_2O_3.	$Fe_2O_3(+FeO)$.	MgO.	CaO.	Na_2O.	K_2O.	Total.
61·70	23·99	0·43	0·40	5·09	8·81	0·17	100·59

This corresponds with orthoclase 0·9, albite 75·1, anorthite 24·0 mol.%. Detailed determinations are given of the optical constants of this and of some other intermediate plagioclases; and the results are applied (pp. 108—122) to a dispersion method of determining the chemical composition of small cleavage flakes of plagioclases by immersion in a mixture of cassia oil and clove oil. L. J. S.

A Peculiar Chlorite-rock from Derbyshire. Cecil S. Garnett (*Min. Mag.*, 1923, **20**, 60—64).—An intrusive sill of olivine-dolerite ("toadstone") at Ible shows along one stratum an alteration into a chlorite-rock. This is soft and friable with a dark olive-green colour, and consists of a confused mass of lamellar and foliated aggregates. The foliated mineral has *d* 2·52, and gave analysis I. The surrounding dolerite is penetrated by numerous small veins filled with a fibrous mineral resembling chrysotile in appearance. This is dark olive-green with *d* 2·37 and gave anal. II. These minerals are compared with epichlorite, and they evidently owe their origin to hydrothermal action following the solidification of the dolerite.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	H_2O.	Total.
I.	37·5	10·4	8·8	10·8	20·8	nil	12·0	100·3
II.	42·7	8·2	13·6	2·8	20·7	nil	11·7	99·7

L. J. S.

The Dartmoor Granite. Alfred Brammall and H. F. Harwood (*Min. Mag.*, 1923, **20**, 20—26, 39—53).—Minute crystals

of brookite and anatase, and rarely of rutile, are found in the sands of several streams and in the red pneumatolysed granite, but were not detected in the fresh grey granite of Dartmoor. They have presumably resulted from the decomposition by pneumatolytic processes of the original titanium-bearing minerals present in the grey granite, namely, ilmenite and sphene, and the more abundant biotite which contains up to 2·04% TiO_2. Biotite from the Haytor granite gave analysis I; after prolonged boiling in strong hydrochloric acid it gave II (partly bleached) and III (completely bleached). The residue is silvery-white and flaky (cf. "bauerite," A., 1913, ii, 868). From it the whole of the titania is readily extracted by a 2% solution of salicylic acid, and much of the silica by sodium carbonate solution.

Nine detailed analyses (TiO_2 0·04—1·11) are given of the different types of granite, which belong to sheets intruded at different periods (IV of the typical "blue granite" of Haytor), two of the associated slates ("killas"), and nine of the porphyritic crystals of felspar (V from Haytor). A red garnet isolated from the granite of Clinkwell Tor gave VI, corresponding with 20·9% of the spessartite molecule.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O (at 110°).	H_2O (> 110°).	Total.
I.	34·65	1·77	20·37	3·49	18·48	0·76	5·25	8·31	0·53	1·00	4·52	100·65 *
II.	76·37	1·23	6·19	0·86	nil	0·87	0·30	3·24	2·53	0·86	7·07	99·52
III.	80·69	0·61	3·62	0·49	nil	0·51	nil	1·40	0·64	6·96	5·10	100·02
IV.	73·66	0·16	13·81	0·21	1·51	0·67	0·45	5·02	2·89	0·41	1·25	100·35 †
V.	65·16	tr.	19·17	0·06	—	0·46	0·14	11·68	3·07	0·10	0·33	100·35 ‡
VI.	37·60	nil	17·78 ?	1·33	29·67	1·31	2·00	—	—	0·13	0·57	99·40 §

* I, also Li_2O 0·32, MnO 0·48, V_2O_3 0·04, F 0·68; BaO, Cr_2O_3, ZrO_2 (?), traces.
† IV, also P_2O_5 0·24, Cl 0·01, MnO 0·06; ZrO_2, BaO, Li_2O, traces; CO_2, S, SrO, nil.
‡ V, also BaO 0·18. § VI, also MnO 9·01.

Some account is given of the heavy minerals (monazite, zircon, spinel, corundum, sillimanite, andalusite, cordierite, etc.) isolated from the normal granites and from the dark patches, the latter probably representing altered fragments of foreign rocks enclosed by the granite. L. J. S.

Meteorite of St. Sauveur, France. A. LACROIX (*Compt. rend.*, 1923, **177**, 561—565).—The material of this stone, which fell on July 10, 1914, at St. Sauveur in Haute-Garonne, is black, dull, and very fine-grained with but few chondrules; *d* 3·66. It closely resembles the Pillistfer, Daniel's Kuil, Khairpur, and Hvittis falls. Polished surfaces show grains of nickeliferous iron and of troilite; and thin sections show that the bulk of the stony material consists of an enstatite poor in iron, with small amounts of clino-enstatite, oldhamite (CaS), maskelynite (a fused felspar, optically isotropic, and with the composition of andesine, An 31%), and very little apatite (as crystals) and graphite. Analyses by Raoult of the portions soluble and insoluble in acid give the following bulk composition:

SiO_2.	Al_2O_3.	FeO.	MgO.	CaO.	Na_2O.	K_2O.	P_2O_5.	Loss at 105°.
33·40	3·29	0·21	17·00	1·12	0·96	0·21	0·17	0·09

Fe.	Ni.	Co.	Mn.	Cr.	Ca.	S.	C.	Total.
34·86	1·62	0·12	0·05	0·08	0·64	5·82	0·10	99·74

This corresponds with the mineralogical composition: pyroxenes 41·25, felspars 13·38, olivine 1·40, nickel-iron 27·49, troilite 14·26, oldhamite 1·15, daubreelite 0·22, apatite 0·34, graphite 0·10%. The metallic portion is present in unusually large amount and is very poor in nickel (Fe : Ni=16 : 1), whilst the enstatite is very poor in iron. L. J. S.

Analytical Chemistry.

A Quantitative Buchner Filter. R. J. Cross (*Ind. Eng. Chem.*, 1923, **15**, 910).—An ordinary Buchner funnel is provided with a glass or porcelain cylinder, which is held by a clamp into which the whole funnel fits, in such a way as to hold the filter firmly down on the perforated plate. The joint between this retaining cylinder and the perforated plate is made to fit accurately, by grinding an annular channel in the surface of the plate, slightly wider than the thickness of the retaining cylinder, the end of which is ground true. On the completion of the filtration, the clamp is loosened and slid back, a watch glass is placed over the cylinder, and the whole filter inverted, the filter and its contents being loosened by blowing through the stem of the funnel. A flat joint with a rubber gasket is used for connexion with the suction flask. [Cf. *J.S.C.I.*, 1923, 1104A.] H. C. R.

An Improved Methyl-orange. James Moir (*J. S. African Chem. Inst.*, 1923, **6**, 69—70).—The indicator proposed is *p*-sulpho-*o*-methoxybenzeneazodimethyl-α-naphthylamine; it changes from orange in alkaline solution to bluish-violet in acid solution, the range of p_H over the change being 4·9 to 3·5. The indicator is slightly sensitive to carbon dioxide by daylight, but not by artificial light. W. P. S.

Bromoxylenol-blue. A True-neutrality Point Indicator. Abraham Cohen (*Biochem. J.*, 1923, **17**, 535).—Bromoxylenol-blue (dibromoxylenolsulphonephthalein), $C_{23}H_{20}O_5Br_2S$, is prepared by adding bromine under constant shaking in the cold to xylenol-blue suspended in glacial acetic acid and keeping over-night. The filtered crystals are recrystallised from dry boiling toluene. It covers the same p_H ranges as bromothymol-blue but possesses the advantage that it is easy to prepare. Bromoxylenol-blue can have its working range halved by the addition of bromo-cresol-purple. The resulting mixed indicator can be used where a blue end-point of Sörensen value about 6·8 is desired in a titration. S. S. Z.

Apparatus for Electrometric Titrations. A. J. Pelling (*J. S. African Chem. Inst.*, 1923, **6**, 40—48).—In the apparatus described and illustrated oxygen is excluded completely from the electrodes during the titration, and the hydrogen is washed before entering the electrode vessel by first passing it through the bulk

of the solution. The apparatus also permits the titration of substances which are decomposed by contact with platinum black saturated with hydrogen. W. P. S.

A Convenient Form of Burette for Exact Gas Analysis. HENRY JERMAIN MAUDE CREIGHTON (*Trans. Nova Scotian Inst. Sci.*, 1919—20, **15**, [2], 115—117).—The burette consists of two parallel limbs connected by a capillary tube through a T-piece with a stop-cock at the top. The larger limb is composed of bulbs connected by constricted portions on each of which there is a graduation mark. The capacity of the upper bulb and of that portion of the parallel limb which is above the top graduation mark is 70 c.c., that of each of the other bulbs is 5 c.c. The parallel limb is a straight tube of 5 c.c. capacity graduated to read each 0·01 c.c. At the base of each limb there is a stop-cock below which are connexions to a common reservoir and pair of levelling tubes. By alternate operation of the lower stop-cocks the major portion of the gas is measured in the large limb and the fraction of 5 c.c. in the small limb. [Cf. diagram, *J.S.C.I.*, 1923, 1045A.] H. HG.

Spectroscopic Methods in Analytical Chemistry. C. AUER-WELSBACH (*Sitzungsber. Akad. Wiss. Wien*, 1922, **131**, II*b*, 339—355; from *Chem. Zentr.*, 1923, iv, 75—76).—An apparatus for the study of spark spectra is described. All elements under normal pressures, with the exception of oxygen, nitrogen, the inert gases, the halogens, arsenic, and the elements of the sulphur group give such spectra with characteristic lines. The limitations of the method are discussed. G. W. R.

Systematic Scheme for the Detection and Separation of the Acids. Z. KARAOGLANOV and M. DIMITROV (*Z. anal. Chem.*, 1923, **63**, 1—10).—The acids are divided into eight groups, the first consisting of those volatile by distillation with acetic acid, viz. carbonic, hydrocyanic, sulphurous, thiosulphuric, hyposulphurous, nitrous, and hypochlorous acids. The vapours are passed through a nitric acid solution of silver nitrate which gives a precipitate with hydrocyanic, hypochlorous, and hydrosulphuric acids; another portion is passed through barium hydroxide solution, which is rendered turbid by carbonic or sulphurous acids, and a third portion through iodide–starch solution, which is turned blue by nitrous or hypochlorous acid. Further portions of the gases from the distillation are then subjected to specific tests for each member of the sub-groups found to be present. The solution in the distilling flask is tested for group II acids (nitric and boric) by means of diphenylamine and turmeric, respectively. A second portion of the same solution is treated with barium and calcium acetates, which precipitate group III acids (sulphuric, hydrofluosilicic, chromic, hydrofluoric, oxalic, iodic, and tartaric). The precipitate is extracted with dilute nitric acid and the precipitate is tested for sulphate (charcoal test), iodate (blue colour with hydrochloric acid, zinc, and starch), and fluosilicate (sulphuric acid and water-drop test). The solution is treated with ammonium acetate

and calcium and barium acetates and the precipitate is heated with sulphuric acid, the gases being passed through barium chloride, then through barium hydroxide solution; a cloudiness in the former indicates hydrofluoric, and in the latter, oxalic acid. If tartaric acid is present, the hydrofluoric and oxalic acids must be removed by means of calcium sulphate in acetic acid solution; the filtrate is then tested for chromic and tartaric acids as usual. The filtrate from the third group is made slightly alkaline with ammonia, and barium acetate is added to precipitate group IV acids (phosphoric, arsenic, and silicic) which are tested for as usual. The group V acids (hydriodic, arsenious, and hydroferrocyanic) are separated from the neutral, diluted filtrate by the addition of lead acetate; hydriodic acid is detected in the precipitate by boiling it with dilute acetic acid and adding chlorine water and starch to the solution after filtration; arsenious acid by separating the lead from this solution and passing hydrogen sulphide through it, and hydroferrocyanic acid by treating the material insoluble in dilute acetic acid with ferric chloride. The filtrate from group VI is made strongly ammoniacal and boiled with a large excess of lead acetate, which precipitates hydroferricyanic acid and the remainder of the arsenious acid. Group VII, consisting of hydrochloric, hydrobromic, and thiocyanic acids, is separated from the filtrate from group VI by addition of nitric acid and silver nitrate. The final filtrate contains only perchloric, chloric, and bromic acids; it is treated with sulphuric acid to separate lead, then with zinc and silver nitrate, which reduces the latter two acids to silver chloride and bromide. The filtrate is boiled with potassium hydroxide and filtered, and the alkaline liquid is boiled with ferrous sulphate, acidified with nitric acid, and treated with silver nitrate; a white turbidity indicates perchlorate. A. R. P.

New Gravimetric Method of Estimating the Relative Humidity of Air with the Help of a Flow Meter. JULIUS OBERMILLER and MARTHA GOERTZ (*Z. physikal. Chem.*, 1923, **106**, 178—190).—A method for estimating the relative humidity of air is described which consists in passing a current of air through a meter to determine the velocity and then dividing the stream into two exactly equal parts, one of which is sent through a phosphoric oxide drying tube and the other is saturated with moisture and passed through a similar drying tube. Both tubes are weighed, and the fraction: increase of weight of the first drier/that of the second drier gives the relative humidity. J. F. S.

Electrometric Titration of Iodate, Bromate, Chlorate, and Ferricyanide with Titanous Sulphate. W. S. HENDRIXSON (*J. Amer. Chem. Soc.*, 1923, **45**, 2013—2017).—Iodate, bromate, and chlorate may be titrated electrometrically with titanous sulphate at the ordinary temperature to an accurate end-point. There is no necessity to titrate back an excess of the reducing agent. The iodate is titrated best in sulphuric acid solution. There is a rise in potential of about 0·25 volt at the commencement of the titration, after which the *E.M.F.* remains steady until the end-

point is reached, when the voltage drops sharply by about 0·3 volt. The change is represented by the equation $5Ti_2(SO_4)_3+2HIO_3+5H_2SO_4=10Ti(SO_4)_2+6H_2O+I_2$. If more titanous sulphate is added after the end-point is reached, the *E.M.F.* falls slowly to about 0·1 volt lower, and then there is a sudden drop of a further 0·1 volt, which indicates the completion of the reaction $Ti_2(SO_4)_3+I_2+H_2SO_4=2HI+2Ti(SO_4)_2$. Bromate may be titrated in sulphuric or hydrochloric acid solution. There is a sharp rise of about 0·3 volt on starting the titration, after which the voltage remains practically steady for some time; it then falls about 0·1 volt rapidly, followed by 0·05 volt slowly. After this there is a sudden drop of about 0·7 volt, which occurs at the end-point. In the case of chlorate, either sulphuric acid or hydrochloric acid may be used. The voltage rises rapidly about 0·5 volt with the first few drops of titanous sulphate, and remains practically constant until the reaction is complete, when it falls suddenly about 0·8 volt. Ferricyanide is titrated in the presence of sulphuric acid, and gives a sharp end-point. It may be estimated as accurately as any other form of iron. In all cases, the results by these methods are extremely accurate. J. F. S.

Estimation of Chlorine, Bromine, and Iodine in Organic Compounds. J. HESLINGA (*Diss. Delft*, 1923, 1—72).—Hydrogenation of organic compounds in presence of various catalysts does not yield a quantitative formation of the halogen acids. Combustion in a stream of ammonia is satisfactory for all classes of organic halogen derivatives except aromatic compounds containing chlorine; the latter are completely decomposed by a mixture of ammonia and hydrogen at combustion temperatures. The decomposition is carried out in an empty quartz tube, of which one part is heated to redness; a plug of cotton wool inserted in the cool end is sufficient to retain all the ammonium halide. Cyanide is usually formed, and is destroyed before estimation of the ammonium halide in solution by boiling with acetic acid.

Very good results are also obtained by combustion in a stream of air containing ammonia, in presence of glowing ferric oxide. The resultant gases are passed through an alkaline sulphite solution, and the halogen is titrated after removal or oxidation of the sulphite.

Both methods are suitable for micro-determinations.

The removal of halogen by means of potassium hydroxide in presence of acetone may be used for estimations in some cases. Aliphatic halogen compounds also are decomposed by potassium hydroxide in alcoholic solution in sunlight in presence of *p*-benzophenone and other aromatic ketones; this method is quantitative for some aliphatic bromine and iodine compounds. S. I. L.

Estimation of Fluorine in Zinc Blende. L. DA ROCHA-SCHMIDT and K. KRÜGER (*Z. anal. Chem.*, 1923, **63**, 29—32).—One g. of finely powdered ore is mixed with 2 g. of freshly ignited and finely powdered quartz powder and 2 g. of carefully washed and ignited silver sand. The mixture is placed in the decomposition

flask and covered with 10 g. of anhydrous chromium trioxide. The flask is connected to a Peligot tube containing 15 c.c. of 50% alcohol saturated with potassium chloride, and a current of perfectly dry air free from carbon dioxide is passed slowly through the apparatus. By means of a dropping funnel, 20 c.c. of anhydrous sulphuric acid (made by evaporating the concentrated acid to two-thirds its bulk and cooling in a desiccator) is allowed to flow into the flask, which is then heated on a paraffin-bath slowly to 130—140°, and maintained at that temperature for three hours. The contents of the Peligot tube are then titrated with $N/10$-sodium hydroxide solution, using cochineal as indicator; 1 c.c. of the standard solution=0·0057 g. of fluorine. For accurate results, absolute dryness of reagents and apparatus is necessary.

A. R. P.

Titration of Hydrofluoric and Hydrofluosilicic Acids in Mixtures containing Small Amounts of Hydrofluosilicic Acid. PAUL H. M. P. BRINTON, LANDON A. SARVER, and ARTHUR E. STOPPEL (*Ind. Eng. Chem.*, 1923, **15**, 1080—1081).—The results of the analyses of the same samples of commercial hydrofluoric acid by Scott's method in three different laboratories showed a wide divergence. This was traced to the effect of the silica in the standard alkali used. The use of sodium hydroxide made from sodium by the action of water vapour, the sodium hydroxide being caught in platinum and stored in bottles lined with ceresin, caused all discrepancies to disappear. The rapidly fading end-points of the cold titration were no longer in evidence, and sharp end-points in which the pink colour persisted for from one to four minutes were obtained. Electrometric titrations showed that in the absence of silica in the standard alkali solution the hydrolysis of the potassium fluosilicate in ice-cold solution was sufficiently slow to allow a ready reading of the cold end-point, whereas in the presence of appreciable amounts of silica in the alkali the change in the hydrogen-ion concentration on keeping was much more rapid, and the end-point colour correspondingly fleeting. If accurate results are desired by this method, estimations of silica must be made in even freshly prepared standard alkali solutions and corrections applied to the figures found for the two acids. The weight of silica added during the titration up to the cold end-point should be multiplied by 2·393 to find the weight of hydrofluosilicic acid to be deducted from that found in the mixture. To find the weight of hydrofluoric acid to be added to that found by analysis, the weight of silica added should be multiplied by 1·991.

H. C. R.

A Simple, Sensitive Process for the Detection of Oxygen by a Biochemical Method. HANS SCHMALFUSS (*Ber.*, 1923, **56**, [*B*], 1855—1856).—The process is based on the observation that a piece of filter-paper impregnated with worm blood and *l*-β-3 : 4-dihydroxyphenyl-α-alanine becomes blackened as the result of melanin formation when exposed to oxygen. The reaction is not influenced by the presence of nitrogen, hydrogen, carbon

monoxide, or carbon dioxide, but bromine, chlorine, hydrogen sulphide, hydrocyanic acid, and sulphur dioxide must be removed. In the presence of 0·9% of oxygen, the paper becomes darkened within three minutes. H. W.

Colorimetric Estimation of Small Amounts of Oxygen. PERCY GEORGE TERRY HAND (T., 1923, **123**, 2573—2576).

Micro-sampling for the Determination of Dissolved Oxygen. R. V. ALLISON and J. W. SHIVE (*Soil Sci.*, 1923, **15**, 489—491).—A modified Winkler apparatus is described for the sampling of liquid media in which dissolved oxygen is to be estimated. G. W. R.

A Rapid Gasometric Method of Estimating Dissolved Oxygen and Nitrogen in Water. H. G. BECKER and W. E. ABBOTT (*Sci. Proc. Roy. Dubl. Soc.*, 1923, **17**, 249—253).—Air dissolved in water is set free by dissolving in the water some highly soluble substances, of which potassium hydroxide has been found the most effective. An apparatus is described in which this fact is applied to the determination of the quantity of air dissolved in water. The water to be examined is saturated in a bulb with potassium hydroxide and the air liberated is measured. The oxygen is then absorbed in alkaline pyrogallol and the residual nitrogen is measured. The total air found by this method is slightly greater than by other methods, due to air in the potassium hydroxide, whilst the oxygen is slightly lower, through incomplete absorption. E. H. R.

A New Method of Estimating Sulphur, Arsenic, and Antimony in Organic and Inorganic Compounds by "Sinter-Oxidation." FRITZ FEIGL and REGINA SCHORR (*Z. anal. Chem.*, 1923, **63**, 10—29).—Sulphur, arsenic, and antimony are quantitatively converted into sulphate, arsenate, and antimonate by heating any organic or inorganic compound containing these elements with twice its weight of a mixture of equal parts of sodium carbonate and potassium permanganate under a layer of the same mixture in an iron crucible for one hour at a low red heat. The residue from this "sinter-oxidation" is boiled with water, the solution cooled and treated with one-half its volume of alcohol, and the insoluble material collected and washed with 30% alcohol. The solution is used for the estimation of sulphur as barium sulphate and of arsenic, either iodometrically or as magnesium ammonium arsenate. The residue is dissolved in hydrochloric acid and a little oxalic acid, and the antimony is estimated iodometrically in strong hydrochloric acid solution. The process is applicable to the estimation of these elements in sulphide, sulpharsenide, and sulphantimonide ores as well as in such organic substances such as phenylthiocarbamide, salvarsan, and arsinic acids. A. R. P.

Estimation of "Sulphonitric" and "Sulphonitrous" Acids. ANDRÉ GRAIRE (*Compt. rend.*, 1923, **177**, 821—823).—The author

discusses the disadvantages of the common methods of analysing sulphuric acid containing nitrous and nitric acids, etc. Nitrometer estimations may give low results owing to the presence of iron and copper salts, which hold back nitric oxide. This fact is demonstrated by oxidising with permanganate the acid remaining in the nitrometer (after displacing the usual nitric oxide formed), then treating with ferrous chloride, and measuring the second volume of nitric oxide formed. This supplementary method may be used to obtain accurate analyses of the acids in question. E. E. T.

The Influence of the Nature and Position of Substituents on the Kjeldahlisation of Aromatic Nitro-compounds. B. M. Margosches and Wilhelm Kristen [with Erwin Scheinost] (*Ber.*, 1923, 56, [*B*], 1943—1950; cf. Margosches and Vogel, A., 1920, ii, 50; 1922, ii, 522).—The authors have greatly extended the scope of their examination of the kjeldahlisation of aromatic nitro-compounds which now includes nitro-phenols, -benzoic acids, -benzyl alcohols, -benzaldehydes, -anisoles, -phenetoles, -benzyl chlorides, nitroanilines, nitroacetanilides, and nitrotoluidines. The substance is treated with sulphuric acid alone or in the presence of potassium sulphate, copper oxide, or mercuric oxide.

Accurate results are obtained in the estimation of nitrogen with *o*-nitrophenol, *o*-nitrobenzoic acid, *o*-nitrobenzaldehyde, *m*-nitroaniline, *m*-nitroacetanilide, *m*-nitrodimethylaniline, and 2 : 6-dinitrophenol by treatment with sulphuric acid alone or in the presence of catalysts or substances which raise the boiling point of the acid.

The substituents may be arranged with regard to their behaviour on kjeldahlisation by sulphuric acid alone in the following classes: (*a*) the substituents, ·OH, ·OMe, $\cdot CO_2H$, and ·CHO, favour the accuracy of the process mainly when they are in the ortho-position to the nitro-group; (*b*) the residues, $\cdot NH_2$, ·NHAc, and $\cdot NMe_2$, have a similar action when in the meta-position; (*c*) the substituents ·Me, $\cdot CH_2\cdot OH$, and $\cdot CH_2Cl$ appear generally to be without influence. The effect of a nitro-group on a second nitro-group could not be established with certainty.

The effect of a substituent on the kjeldahlisation of the nitro-group appears to be explicable by the increase or diminution of the reactivity of the nitro-group induced by the presence of the substituent. H. W.

The Sulphate-Molybdate Method of Estimating Phosphoric Acid. V. A. Beckley and A. Marais (*J. S. African Chem. Inst.*, 1923, 6, 35—39).—When this method is used, it is recommended that the phosphomolybdate precipitate be washed with 3% sodium nitrate solution, using 20 c.c. each time; the precipitate should be disturbed as little as possible. After the fifth washing, each quantity of filtrate should be tested and as soon as it yields a red coloration on the addition of 0·05 c.c. of *N*/10-sodium hydroxide solution, using phenolphthalein as indicator, the precipitate may be considered to be washed completely. W. P. S.

[Estimation of Phosphoric Acid and Potassium in Soils, etc.] H. F. L. Bischoff and B. de C. Marchand (*J. S. African Chem. Inst.*, 1923, **6**, 53—60).—The authors have investigated the effect of certain conditions, etc., on the accuracy of the estimation of potassium and phosphoric acid in soils and fertilisers. In the estimation of available potash in soils, ignition of the soil extract does not cause loss of potassium and the quantity of citric acid-soluble phosphoric acid found in basic slag is not affected appreciably when considerable variations are made in the time of shaking or in the volume of citric acid solution used. The solubility of bonemeal and rock phosphate in citric acid solution increases with the fineness of the material; samples of these substances should be analysed in the state in which they are received, and should not be ground previously to analysis. W. P. S.

Estimation of Minute Quantities of Arsenic. III. O. Billeter and E. Marfurt (*Helv. Chim. Acta*, 1923, **6**, 771—779).—Previous work on the detection of minute quantities of arsenic (cf. A., 1919, ii, 32; this vol., ii, 335) left two points still in an unsatisfactory state. The destruction of organic matter is not absolutely complete and the quantitative estimation of the arsenic by comparison of the mirrors is imperfect. The first difficulty may be overcome as follows. The organic matter to be tested is treated with fuming nitric acid and sulphuric acid as before, the nitric acid driven off, the sulphuric acid solution neutralised with sodium carbonate, and evaporated to dryness. There are then added, for 20 g. of organic matter, 2 g. of potassium perchlorate and 0·3 g. of potassium bromide and the mixture is transferred little by little to a platinum crucible heated to redness, finishing with a gentle fusion. The distillation with sulphuric acid is then carried out as before. The sensitivity of the Marsh apparatus is increased by forming the mirror in a capillary tube at a point which will just prevent the passage of a platinum wire 0·3 mm. thick.

For the estimation of the arsenic in the mirror, the portion of tube containing the mirror is treated with five to ten times the theoretical quantity of iodine solution and a little sodium hydrogen carbonate in a stoppered test-tube. After two or three hours the arsenic has all dissolved and the excess of iodine is titrated with thiosulphate, using starch as indicator. The solutions used are 0·005 to 0·01N, and the necessary degree of refinement is obtained by using special burettes, one of 0·5 c.c. capacity graduated to 0·002 c.c. and one of 2 c.c. graduated to 0·01 c.c. for larger quantities. Accuracy to 0·03 m.mg. of arsenic is claimed by this method. Experiments to determine the proportion of the original arsenic recovered in the mirror showed that the yield is greater the smaller the quantity of arsenic being dealt with. Starting with 100 m.mg. of arsenic, 92·5% was found in the mirror, whilst with 1 m.mg. or less, 99% was found. E. H. R.

Simple Method of Estimating Arsenic. Poussigues (*Ann. Chim. Analyt.*, 1923, **5**, 263—267).—Copaux's method of estimating phosphates by measuring the volume of the oily yellow

liquid formed by their interaction with sodium molybdate solution in the presence of sulphuric acid and ether is slightly modified and extended to arsenic. Nitric acid (*d* 1·20) is used instead of sulphuric acid and the ether must be free from alcohol. A special graduated tube similar to a Gerber milk tube but larger in size is used for the estimation, and the liquid is deposited in the graduated end by centrifuging. The apparatus is calibrated by testing a solution of known arsenic content and a correction is applied for the solubility —which is considerable—of the oily liquid in the acid layer. If 100 c.c. of liquid, corresponding with 1 g. of the mineral, are taken, minerals containing less than 1·16% of arsenic give no oily deposit owing to the solubility of the latter, but this difficulty can be overcome by suitably concentrating the solution before testing. The density of the aqueous phase must be kept low or the yellow liquid will not sink. The presence of metals does not affect the results, but in the presence of antimony the mineral should be dissolved in hydrochloric and tartaric acids. Citric acid, alcohol, and too great excess of sulphuric acid are harmful, and phosphoric acid must be absent. Specimen analyses given agree well with gravimetric analyses of the same samples. H. C. R.

The Estimation of Arsenic as Silver Arsenate. W. Eschweiler and W. Röhrs (*Z. angew. Chem.*, 1923, **36**, 464—466).—The arsenate solution, obtained either by fusion of the material with sodium hydroxide and nitrate or by oxidation of an ammoniacal arsenic sulphide solution by means of hydrogen peroxide, is acidified with nitric acid and carefully neutralised to methyl-orange with ammonia. Two g. of ammonium nitrate and 1 g. of ammonium acetate are added, and the solution is heated to boiling. Silver nitrate solution is added drop by drop until the precipitate coagulates and settles, leaving the supernatant liquid quite clear. The precipitate is collected, washed with cold water, and either heated at 500° and weighed as Ag_3AsO_4 or dissolved in nitric acid and its silver content estimated by titration with potassium thiocyanate. If chlorides are present, the precipitate is dissolved in nitric acid and, after filtering off the silver chloride, reprecipitated as before. Large quantities of sulphates cause the results to be too high; addition of several g. of potassium nitrate prevents this interference. [Cf. *J.S.C.I.*, 1923, 1046A.]
A. R. P.

Estimation of Arsenic in Foods. R. M. Hann (*J. Assoc. Off. Agric. Chem.*, 1923, **7**, 48—54).—The addition of potassium iodide is recommended in the estimation of arsenic by the Gutzeit method in order to ensure complete evolution of the arsenic. Hydrochloric acid may be used in place of sulphuric acid. W. P. S.

Direct Estimation of Arsenic in Toxicology. J. Lewis (*J. S. African Chem. Inst.*, 1923, **6**, 65—68).—In the estimation of arsenic in toxicological specimens by Green's method (A., 1920, ii, 634) equally trustworthy results are obtained whether the organic matter is destroyed by evaporation with sulphuric acid and nitric

acid or the material simply disintegrated by boiling with dilute sulphuric acid without oxidation. In both cases, the loss amounts to about 0·1 mg. when dealing with 1 mg. quantities of arsenic trioxide. W. P. S.

The Separation of Arsenic from Antimony and Tin. LUDWIG MOSER (*Z. anal. Chem.*, 1923, **63**, 40—41).—A criticism of Järvinen's paper (this vol., ii, 254) in which attention is directed to the earlier work of Moser and Ehrlich (this vol., ii, 315) showing that arsenic trichloride is removed completely from a solution saturated with hydrogen chloride by heating on a water-bath whilst passing a current of air through the liquid. The reduction of arsenic acid to arsenious acid by ferrous sulphate is complete only in strong hydrochloric acid solutions. Järvinen's statement that arsenic acid is volatile from hydrochloric acid solutions is incorrect; potassium chlorate does not oxidise arsenious to arsenic acid completely in these solutions, and it is the unoxidised portion of the arsenic that is volatilised. A. R. P.

Microanalytical Estimation of Carbon and Hydrogen by Pregl's Method. A. FRIEDRICH (*Z. angew. Chem.*, 1923, **36**, 481—482).—Too large an increase in weight in the absorption vessels may be traced to impurities given off by the rubber connexions or contained in the oxygen used. The rubber connexions should be reduced to a minimum, and should be previously washed for two hours in hot sodium hydroxide (40—50%), then washed free from alkali, and finally steamed out for two hours. Impurities in the oxygen may be removed by passing the gas over red-hot copper oxide and absorbing any carbon dioxide formed with 50% sodium hydroxide. New absorption vessels tend to lose slightly in weight when wiped with a moist cloth and should be boiled out before being used for the first time. Using lead peroxide asbestos, as described by Pregl, the combustion tube and contents require to be heated to redness for only two to three hours before use, and not for several weeks, as commonly supposed. W. T. K. B.

Analysis of Combustible Gases. ENRIQUE HAUSER (*Bull. Soc. chim.*, 1923, [iv], **33**, 1141—1232).—A lecture delivered, 23rd May, 1922, before the Société chimique de France. H. J. E.

The Application of Micro-analysis to the Elementary Analysis of Fuels. H. GAULT and MAURICE NICLOUX [with G. PFERSCH and R. GUILLEMET] (*Bull. Soc. chim.*, 1923, [iv], **33**, 1299—1304).—In carrying out estimations of the carbon and hydrogen content of a series of bituminous schists by the ordinary methods, inconsistent results were obtained. The method of micro-analysis was therefore tried, the quantities of material used being from 3—5 mg., and this gave concordant results; moreover, a considerable saving of time was effected. The authors are of opinion that these advantages would be gained by using the method in other cases of fuel analysis. H. J. E.

The "Pyro-Tannic Acid" Method for Estimating Carbon Monoxide in Blood and Air. R. R. SAYERS, W. P. YANT, and G. W. JONES (*U.S. Bur. Mines Repts. Investigations*, 1923, No. 2486; cf. Sayers and Yant, A., 1922, ii, 868).—Blood-standards not being permanent, standards are prepared from pigments for use in the method of estimation of carbon monoxide in blood whereby normal blood forms a grey suspension but blood containing carbon monoxide a light carmine precipitate when treated in aqueous dilution with a mixture of tannic acid and pyrogallol. Estimations with blood are accurate to $\pm 5\%$; calculations therefrom of the carbon monoxide content of air are accurate to 0·005% of the total volume when not more than 0·05% is present, or 0·03% when 0·18% is present.

CHEMICAL ABSTRACTS.

The Residue from Silica in Rock Analysis. M. AUROUSSEAU (*J. Washington Acad. Sci.*, 1923, **13**, 330—332).—The residue which remains after silica (obtained in the usual course of analysis) has been treated with hydrofluoric acid is usually quite small in quantity. The author has examined such a residue obtained during the analysis of a silicic andesite; it amounted to 0·52% of the mineral and contained Al_2O_3 12·7%, Fe_2O_3 24·7%, MgO 15·8%, TiO_2 30·0%, and SO_3 8·0%, together with small quantities of calcium, phosphoric acid, and manganese.

W. P. S.

Separation and Estimation of Potassium and Sodium. A Perchlorate Precipitation Process using Normal Butyl Alcohol. G. FREDERICK SMITH (*J. Amer. Chem. Soc.*, 1923, **45**, 2072—2080).—A method has been developed for the separation and estimation of sodium and potassium, which depends on the precipitation of potassium perchlorate from aqueous solution by the addition of a comparatively large volume of *n*-butyl alcohol. The method of procedure is as follows. The mixed chlorides of sodium and potassium, which must be free from sulphate, are evaporated to dryness with an excess of perchloric acid. Two or three c.c. of water are added and the perchlorate dissolved by heating; then 65 or 100 c.c. of *n*-butyl alcohol containing 0·5—1% of perchloric acid, the larger volume being taken when 3 c.c. of water are required to dissolve the perchlorates, are heated to boiling and added slowly with vigorous stirring to the perchlorate solution. This effects the precipitation of the potassium perchlorate, and after all has been precipitated the whole is gently boiled for half a minute and cooled to room temperature. The precipitate is collected on a Gooch crucible, washed with 10 portions of 1—2 c.c. of the precipitating solution, dried at 125—250°, cooled, and weighed. The filtrate and washings are evaporated to dryness and the sodium is estimated as sulphate. This process is rapid and gives excellent results. The solubility of potassium chlorate in anhydrous *n*-butyl alcohol, and in that containing various quantities of water and perchloric acid, has been determined at 25°. The amount dissolved is very small; the quantity dissolved in the solution used for precipitation is only 1 mg. per 100 c.c.

J. F. S.

Estimation of the Titratable Alkali of the Blood with Dinitrosalicylic Acid. JAMES B. SUMNER and ROGER S. HUBBARD [with LUCY L. FINNER] (*J. Biol. Chem.*, 1923, 56, 701—709).—Greenwald and Lewman's method (this vol., ii, 87) has been modified, dinitrosalicylic acid being used in place of picric acid. This has the advantage that the total dinitrosalicylic acid in the filtrate may be readily estimated colorimetrically by means of the coloration produced with ferric chloride. E. S.

Comparative Tests of Various Volumetric Methods for the Estimation of Sodium Sulphide. ANON (*Chem. Ztg.*, 1923, 47, 752—753).—Results obtained by the gravimetric method (oxidation with bromine water followed by precipitation of the liquid with barium chloride) of estimating sodium sulphide in various preparations of the salt were compared with those obtained by the following five volumetric methods: (1) Direct titration with iodine of the slightly acidified solution, (2) addition of excess of iodine to the acid solution followed by titration of the excess with thiosulphate, (3) direct titration without acidifying, (4) addition of excess of iodine without acidifying, followed by titration with thiosulphate, (5) direct titration with iodine in the presence of 0·5—2·0 g. of sodium hydrogen carbonate. Method (1) gave the most satisfactory results, methods (3) and (4) were quite good, but not so exact as (1), method (2) gave low and method (5) high results. The presence of carbonate up to 4% has practically no influence on the results obtained without acidifying, whereas 10% increases the sulphide figures by 1·2%. A. R. P.

The Micro-estimation of Magnesium. ST. GADIENT (*Helv. Chim. Acta*, 1923, 6, 729—733).—The method is essentially that of Hammett and Adams (A., 1922, ii, 587), modified in some of its details. Exact directions for carrying out the estimation are given. When estimating magnesium in serum by this method, it is unnecessary first to remove the albumin. [Cf. *J.S.C.I.*, 1923, Nov.] E. H. R.

The Conductometric Titration of Alkaloids. W. D. TREADWELL and S. JANETT (*Helv. Chim. Acta*, 1923, 6, 734—743).—The alkaloids brucine, quinine, narcotine, and morphine can be titrated accurately with hydrochloric acid by the conductometric method; caffeine is too weak a base to give a distinct break in the titration curve. To avoid the formation of non-conducting layers at the electrodes of the titration cell, when using direct current, a commutator was used giving alternations of 4—8 per second, and the solution was kept stirred with a current of nitrogen. The indicator was a high-resistance millivolt meter shunted between the battery and the commutator. The current used is a few milliamperes with an *E.M.F.* of eight volts. During titration, the titration curve, representing the change of current strength, rises gradually, flattening somewhat as the end-point is approached, and rises sharply as soon as free acid is present in solution. The break in the curve is quite sharp. E. H. R.

The Estimation of Zinc by Schaffner's Method with Repeated Precipitation of the Iron. C. Boy (*Chem. Ztg.*, 1923, **47**, 758).—In Schaffner's method for titrating zinc with sodium sulphide, the proportions of free ammonia in assay and standard must be the same. If the iron is precipitated several times with ammonia to remove the zinc completely, the amounts of free ammonia in a series of assays will vary. To rectify this, the solutions should be boiled until all free ammonia is expelled and a cloudiness due to precipitated basic zinc chloride is produced; 5 c.c. of 1 : 1-hydrochloric acid are added, followed by 15 c.c. of ammonia, and the whole is set aside over-night uncovered. Approximately equal quantities of ammonia will be contained in all the trials in the morning. A. R. P.

The Quantitative Treatment of Metals of the Ammonium Sulphide Group. G. Luff (*Z. anal. Chem.*, 1923, **63**, 32—39).—Manganese may be separated from iron and aluminium by one precipitation with ammonia, zinc and nickel by two, and cobalt by three precipitations by operating as follows: Ten grams of ammonium chloride are added for every 100 c.c. of solution, followed by ammonia until neutral; the solution is boiled for fifteen minutes, then treated with ammonia drop by drop until it reacts just alkaline to litmus, and filtered. The precipitate is washed with a hot, dilute, faintly ammoniacal solution of ammonium nitrate, and, if necessary, redissolved in hydrochloric acid and the process repeated. A single precicitation of iron and aluminium by means of pyridine serves to separate these elements from manganese satisfactorily; in the presence of zinc, nickel, and, especially, cobalt, the precipitate contains appreciable quantities of these elements and should be redissolved in acid and reprecipitated with ammonia. The pyridine precipitation is carried out in the same manner as that by means of ammonia, 5 c.c. of pyridine being added to each 100 c.c. of solution containing 10 g. of ammonium chloride. A. R. P.

[Estimation of Manganese and of Zinc as Sulphates.] W. F. Hillebrand (*Z. anal. Chem.*, 1923, **63**, 41—42).—It is pointed out that contrary to Huber's statement (A., 1922, ii, 398) manganese sulphate is slowly decomposed at 600° and that the heating should be conducted at 450—500° (cf. Blum, A., 1912, ii, 1214). Gutbier and Staib's observation (A., 1922, ii, 396), that zinc sulphate, heated with an excess of sulphuric acid, tenaciously retains traces of free acid, is confirmed. A. R. P.

Volumetric Estimation of Iron. A New Method of Reduction. P. F. Thompson (*Proc. Australasian Inst. Mining Met.*, 1922, N.S., No. **47**, 343—346).—Zinc sulphide emulsion is prepared by passing hydrogen sulphide, with occasional additions of ammonia solution, into a solution of 100 g. of zinc sulphate in 2 litres of water until precipitation is complete, decanting, washing the precipitate a few times with very dilute sulphuric acid, and diluting to 2 litres. To a hot solution of ferric iron in dilute sulphuric acid, the emulsion is slowly added until a decided turbidity is obtained; the liquid

is boiled until a drop, tested with thiocyanate, indicates complete reduction. If a brown sulphide is formed, the solution is filtered. After being boiled with dilute sulphuric acid and a little marble until the sulphur has become granular and hydrogen sulphide removed, the ferrous iron is estimated in the usual way.

CHEMICAL ABSTRACTS.

Quantitative Separation of Uranium from Thorium and the Rare Earths in Pitchblende by Means of Sodium Thiosulphate. W. RISS (*Chem. Ztg.*, 1923, **47**, 765—766).—The pitchblende is dissolved in nitric acid, the insoluble matter separated, and the filtrate evaporated to dryness several times to remove the acid. The residue is dissolved in water, exactly neutralised with dilute ammonia, and sodium thiosulphate added in excess. The solution is boiled for ten minutes, and left for twenty-four hours. If sufficient thiosulphate has been used, the supernatant liquid is almost colourless, and the precipitate contains all the thorium, the greater part of the uranium, and small quantities of rare earths (chiefly cerium). To separate the rare earths completely, the precipitate is redissolved in hydrochloric acid and reprecipitated. The precipitate is then dissolved in hydrochloric acid and the thorium precipitated with oxalic acid, ignited, and weighed as thorium oxide, which should be pure white. To determine uranium, the oxalic acid in the filtrate is destroyed by evaporating to dryness and heating the residue with concentrated sulphuric acid. The uranium can then be precipitated with ammonia. The filtrate, after the separation of the thiosulphate precipitate, is tested for thorium, and if this is absent, precipitated with oxalic acid, which removes the rare earths. Iron is precipitated with ammonium carbonate, and the rest of the uranium with ammonia, the two uranium precipitates being ignited and weighed together.

H. C. R.

Colorimetric Estimation of Small Quantities of Bismuth. L. CUNY and G. POIROT (*J. Pharm. Chim.*, 1923, **28**, [vii], 215—223). —The orange-coloured colloidal solutions of quinine iodobismuthate given by a standard bismuth solution and the solution to be estimated are compared colorimetrically. For the standard solution, 2·23 g. of bismuth oxide are dissolved in, and made up to 1 litre with, 10% nitric acid, and 25 c.c. of this solution are added to 175 c.c. of 10% nitric acid and made up to 1 litre with distilled water. To 5 c.c. of this solution are added 3 c.c. of a clear, 10% solution of gum arabic, then 1 c.c. of a solution containing 1 g. of quinine hydrate and 5 c.c. of 10% nitric acid per 100 c.c., and finally 1 c.c. of a 5% solution of potassium iodide. The solution under estimation, with additions as above, is compared with a thickness of 5 mm. of the standard, and the thickness required for matching the colour is arranged, by suitable dilution, to be between 4 and 7 mm. In a series of test estimations the maximum error was 3·5%. The presence of various substances, *e.g.*, hydrochloric, sulphuric, and acetic acids, and various metallic salts, vitiates the results. Coloured precipitates or colloidal solutions are given by salts of the following

metals: silver (yellow), mercurous (dirty green, changing to red), mercuric (yellow), lead (light yellow), stannous (orange; but no reaction in presence of gum arabic), antimony (dark yellow), copper (brown), ferric (liberation of iodine and formation of quinine periodide), cadmium (white). Salts may also cause flocculation of the colloidal quinine iodobismuthate. W. T. K. B.

Tests of Officinal Vaselin, Liquid Vaselin, Paraffin, and Light Petroleum: Action of Cold Concentrated Sulphuric Acid. F. RICHARD (*J. Pharm. Chim.*, 1923, [vii], **28**, 209—214).—The author suggests the abolition from the French "Codex" of the vague directions for testing pharmaceutical vaselins, etc., with 60% sulphuric acid. It is preferable to triturate or agitate the material with twice its weight of cold concentrated sulphuric acid, after an hour's contact, with which no more than a pale yellow coloration should be obtained. The material should also have a neutral reaction to litmus and leave no ponderable ash or residue when calcined or evaporated on the boiling water-bath. W. T. K. B.

Use of the Salts of the Arylsulphonhalogenoamides in the Estimation of Phenols. ELWYN ROBERTS (T., 1923, **123**, 2707—2712).

The Effect of Phenol in the Estimation of Reducing Sugars by the Picramic Acid Methods. H. C. SWEANY (*J. Lab. Clin. Med.*, 1923, **8**, 572—578).—Phenol, present at a concentration of 1 in 4,000, causes a two- to three-fold increase of colour in the estimation of sugar by Lewis and Benedict's or Benedict's method. The phenols present in normal blood cause a 10% error in the estimation of blood-sugar by the former, but not by the latter, method. It is likewise essential to eliminate phenols from urine before estimating the sugar by picramic acid methods which are also inapplicable in the case of sugar solutions preserved by phenols and many related substances. The phenol may possibly react with the decomposition products of dextrose to give a product which either is coloured or becomes reduced to picric or picramic acid.

CHEMICAL ABSTRACTS.

The Chemical Analysis of Cotton. I. The Absorption of Methylene-blue by Cotton. CONSTANCE BIRTWELL, DOUGLAS ARTHUR CLIBBENS, and BERT P. RIDGE (*J. Text. Inst.*, 1923, **14**, T, 297—313).—An examination has been made of the relations between the absorption of methylene-blue by bleached cotton and (1) the ash content of the cotton, in view of the work by Rona and Michaelis (A., 1920, ii, 475), (2) the origin of the raw cotton, and (3) the nature of the bleaching process. Two analytical methods are described. The first, a colorimetric method, employs solutions of methylene-blue hydrochloride about 0·05 to 0·25 millimole per litre, made by diluting a solution containing 10 millimoles per litre, which is standardised by titration with titanous chloride. The cotton is shaken with the dye solution (usually 0·4 millimole per l.) for eighteen hours in a stoppered bottle and then the free liquid is compared in a Kober-Klett colorimeter with a standard about half

as strong as the original (0·2 millimole per l.). The weight of cotton is so chosen that the colorimeter reading is nearly the same for the test as for the control, say, 17—23 as against 20, since the depths of colour of methylene-blue solutions are not strictly proportional to their concentrations. For normally-bleached American cotton, the quantity required, under the above conditions, is about 1·5—2 g. for 50 c.c. of dye; of bleached Egyptian cotton, 0·8—1 g. is sufficient.

The second analytical method is for more concentrated solutions of dye, about 2·5 to 3·5 millimoles per litre. The methylene-blue solutions are titrated with a solution of naphthol-yellow-S, which gives a reddish-brown precipitate, the supernatant liquid changing ultimately from blue to yellow. The yellow solution can be standardised against methylene-blue, or the dye itself, $C_{10}H_4O_8N_2SNa_2$, can be recrystallised from dilute alcohol and accurately weighed out. In order to use a high proportion of cotton relatively to the volume of methylene-blue, and to recover most of the liquid for titration, the cotton is placed in the bottom of a wide tube constricted in the middle, left immersed in the dye for eighteen hours, and then the tube is inverted into a wider tube and centrifuged for fifteen to thirty seconds at 1,500 r.p.m. Using about 2·5 g. of cotton and 15 c.c. of dye, it is possible to recover 12—13 c.c. of clear liquid for titration. The approach of the end-point when adding naphthol-yellow-S is detected by observing the colour of a drop of the liquid on a glass rod, and thereafter the tube is centrifuged after each addition until the blue gives place to yellow.

The first important result obtained is the proof that an increase in the ash content of the cotton, or, more strictly, in the alkalinity of the ash, causes an increased adsorption of methylene-blue, other factors being constant. In order to study other effects, it is necessary, therefore, to wash the cotton submitted for examination under controlled conditions before further tests. Agitation with 0·1*N*-acid for two or three hours, followed by washing with distilled water, finally on a centrifuge, until the washings are indifferent to an iodide–iodate–starch mixture, is recommended. A second result of general importance is the proof that Egyptian cotton, although bleached and washed by the same process, absorbs distinctly more methylene-blue than American cotton, even if the Egyptian cotton is grown in America. The other results have significance in the practice of bleaching, but it may be said that, from cotton material of known origin, the methylene-blue absorption offers a method of quantitatively following the progressive purification of cotton cellulose during bleaching, and ultimately of measuring the success of the bleaching operation, that is, of determining whether "over-bleaching" or inefficient scouring have occurred. J. C. W.

Titrimetric Estimation of Formic Acid. BROR HOLMBERG and SVEN LINDBERG (*Ber.*, 1923, **56**, [*B*], 2048—2052).—The authors take advantage of the fact that when a formate reduces mercuric chloride to the mercurous form, one equivalent of hydrogen chloride is liberated. The solution to be tested is neutralised, excess of standard baryta added, and boiled for about an hour to

complete the oxidation of the formate. Then sodium or potassium bromide solution is added to ensure the precipitation of the calomel, the solution is made acid with a known amount of hydrochloric acid, and boiled to expel the carbon dioxide. Finally, the solution is again neutralised with baryta. The difference between the acid added and the sum of the two portions of baryta obviously gives the amount of acid formed and is equivalent to the formate reduced. The method gives good results and can be used in the presence of acetates. H. H.

Estimation of Amino-acids by Electrometric Titration. ERIK M. P. WIDMARK and ERIK L. LARSSON (*Biochem. Z.*, 1923, **140**, 284—294).—Amino-acids behave during electrometric titration with strong alkali as weak acids devoid of amphoteric character. By measuring the increasing conductivity of amino-acid solutions during the gradual addition of small volumes of 1·0*N*-sodium hydroxide and plotting the results, it was found that the increase was linear up to a point corresponding with complete neutralisation, beyond which a much more rapid increase was noted. The amount of alkali used up to the point of break in continuity serves as a means of estimation. Dibasic acids show two such points, one corresponding with each carboxyl group. The method is applicable to dipeptides and to all the amino-acids examined with the sole exception of arginine. J. P.

Estimation of Small Quantities of Oxalic Acid. Application to Urine. J. KHOURI (*Ann. Chim. Analyt.*, 1923, [ii], 5, 205—207).—The solution containing oxalic acid is evaporated, the residue obtained is treated with a known volume of alcoholic carbamide solution and again evaporated; the excess of carbamide is then extracted with ethyl alcohol or amyl alcohol, and, after the alcoholic solution has been evaporated, estimated by the hypobromite method. The difference between this quantity and that present originally (as estimated in another portion of the carbamide solution) gives the amount of carbamide combined with the oxalic acid as carbamide oxalate, $2CO(NH_2)_2,C_2H_2O_4$. In the case of urine, the oxalic acid which may be present is extracted with ether, the solvent is evaporated, and the residue obtained treated as described. W. P. S.

Estimation of *p*-Sulphamidobenzoic Acid in "Saccharin." O. BEYER (*Chem. Ztg.*, 1923, **47**, 744).—An investigation into the degree of accuracy of methods of estimating *p*-sulphamido-benzoic acid in commercial "saccharin" showed that the German official method (A., 1920, ii, 518) is capable of showing quantities of 1% and upwards when 10 g. of the sample are taken for analysis and may be considered sufficiently accurate for practical purposes. Hefelmann's method does not give such good results, and is not so convenient, because saccharin does not dissolve so readily in the 73% sulphuric acid prescribed as in the 25% hydrochloric acid prescribed in the official method. H. C. R.

Detection of Ethyl Phthalate in Brandy. S. Eilles (*Z. Unters. Nahr. Genussm.*, 1923, **45**, 379—381).—In the presence of concentrated sulphuric acid, pyrogallol gives a violet coloration with ethyl phthalate. In testing plain brandies, 20—50 c.c. of the sample are treated with 5 drops of 15% sodium hydroxide and evaporated to dryness before the test is applied. In the case of products containing sugar and extract matter such as formic acid, 20—50 c.c. of the sample diluted with an equal volume of water are extracted with 25 c.c. of light petroleum (b. p. 30—50°). Tinctures should be treated with the minimum necessary quantity of lead acetate and filtered before dilution and extraction with light petroleum. The light petroleum extract is evaporated to dryness without the addition of sodium hydroxide and the test applied to the residue. The test is sensitive to 0·01% of ethyl phthalate in straight brandies and to 0·1—0·4% in cases in which extraction with light petroleum is necessary. H. C. R.

Estimation of Phenolphthalein. S. Palkin (*J. Assoc. Off. Agric. Chem.*, 1923, **7**, 14—17).—The iodine method described previously by the author yields fairly trustworthy results, but there is a tendency for the figures obtained to be too low. An alternative method, in which the phenolphthalein is precipitated from its alkaline solution by the addition of hydrochloric acid and then extracted with ether and weighed, gives results which are slightly too high. W. P. S.

Estimation of Phenylcinchoninic Acid (Cinchophen, Atophan). William Rabak (*J. Assoc. Off. Agric. Chem.*, 1923, **7**, 32—34).—To estimate phenylcinchoninic acid in tablets or powders, 1 g. of the sample is extracted repeatedly with hot alcohol, the alcoholic extracts are filtered, the filtrate is treated with an excess of $N/10$-sodium hydroxide solution, and then titrated with $N/10$-hydrochloric acid, using phenolphthalein as indicator. Each c.c. of $N/10$-alkali solution is equivalent to 0·02491 g. of phenylcinchoninic acid. W. P. S.

Gravimetric Method for Estimating the Hydroxyl Value and the Acetyl Value [of Oils]. E. B. Elsbach (*Chem. Umschau*, 1923, **30**, 235—237).—The oil is heated at 100° in a flask provided with a tube sealed through the side of the neck and bent at right angles inside the flask, so that it passes downwards and terminates in a constriction close to the bottom of the flask. Dry carbon dioxide or nitrogen is passed through this tube into the oil, which is heated until constant in weight, 4—6 c.c. of acetic anhydride are then added, and the flask is again heated, a reflux condenser being used. When the acetylation is complete, the reflux condenser is removed and dry carbon dioxide again passed through the heated liquid until the excess of acetic anhydride is removed. If p denotes the percentage increase in weight, based on the original weight of the oil, the hydroxyl value is $p \times 13{\cdot}354$ and the acetyl value $p \times 13{\cdot}354/1+p/100$. The latter, being based on the weight of acetylated oil, is always less than the former. The determination takes two and a half to four hours. H. C. R.

Estimation of Formaldehyde in Presence of Substances Found in Formalin. P. Borgstrom (*J. Amer. Chem. Soc.*, 1923, **45**, 2150—2155).—The iodometric method (this vol., ii, 590) can be used for the estimation of formaldehyde in the presence of methyl alcohol, formic acid, or pure methylal, but not in the presence of acetone or ethyl alcohol. The hydrogen peroxide method (*loc. cit.*) can be used if methyl alcohol, ethyl alcohol, formic acid, or methylal is present; if acetone is present in concentration equal to that of the formaldehyde, the figure obtained for the latter will be about 2% high. Methyl alcohol, ethyl alcohol, formic acid, or methylal does not affect the estimation of formaldehyde by the neutral sulphite method (*loc. cit.*), but acetone introduces an error which cannot readily be corrected. W. S. N.

Estimation of the Purity of Vanillin. S. B. Phillips (*Analyst*, 1923, **48**, 367—373).—A volumetric method of estimating vanillin is described depending on the formation of an anhydro-derivative by the interaction of vanillin and *p*-toluidine dissolved in 80% alcohol. This compound contains the original hydroxyl group of the vanillin, and is therefore soluble in alkali, giving a yellow solution. A measured excess of standard alkali is added, followed by a comparatively large volume of cold water. The addition of standard acid first neutralises the excess of alkali, and then liberates the anhydro-derivative from its sodium salt. The first drop of acid which liberates the derivative gives a yellow turbidity, the free derivative being practically insoluble in the liquid phase. The volume of alkali required for the titration of the vanillin is thus obtained. Accurate results are obtained when benzoic acid is present as an adulterant in quantities up to 10%, but with higher percentages of acid it is advisable to use a gravimetric method. No sample of first class vanillin was found to contain more than 1% of acid (as vanillic acid) although some of the samples had been kept in cardboard containers for ten years. The gravimetric method suggested comprises the precipitation of vanillin as the semicarbazone from dilute acetic acid solution. The precipitate is easy to wash and filter, and may be dried in a water oven for six to eight hours without losing a weighable quantity by volatilisation. The vanillin may be separated from impurities such as piperonal by dissolving the semicarbazone in ammonium hydroxide solution. Vanillinsemicarbazone, by virtue of its hydroxyl group, forms a soluble ammonium salt giving a yellow solution, whilst piperonalsemicarbazone is insoluble. Test analyses in which piperonal was added to vanillin gave results agreeing with the actual percentage present to within 1 part in 450 parts. Details of the purification of the vanillin used in this work and of the *p*-toluidine used in the volumetric method are given. The oxidation of samples of purified vanillin exposed to air, moisture, and light was practically negligible. With vanillin in solution, however, oxidation proceeds much more rapidly, whilst solutions of vanillin in alkali behave similarly to alkaline pyrogallate solution. The following corrected melting points are

given: vanillinsemicarbazone, 232°; piperonalsemicarbazone, 218°; vanillin *p*-nitrophenylhydrazone, 223°; vanillin-*p*-bromophenylhydrazone, 148°. H. C. R.

"Permutite" as a Reagent for Amines. JOHN C. WHITEHORN (*J. Biol. Chem.*, 1923, **56**, 751—764).—Bases with a dissociation constant of not less than 5×10^{-9} (for example, alkylamines, basic amino-acids, histamine, tyramine) may be removed almost completely from neutral, and less completely from acid or alkaline, solution in water by shaking with, or preferably by filtration through, permutite. Other solvents (ethyl alcohol, amyl alcohol, ether) may also be employed, but the same bases are not necessarily removed as from water. Recovery of the bases is best effected by treatment of the permutite with a saturated solution of potassium chloride. A study of the reaction with ammonium chloride has shown that the mass law is obeyed; in the expression $[NH_4Cl][Na\ permutite]=K[NH_4\ permutite][NaCl]$, K has a value of 0·75. The temperature coefficient of the reaction between 0° and 17° is 1·6.

A colorimetric method for the estimation of adrenaline, based on its removal from interfering substances by means of permutite, is being worked out. E. S.

Determination of the Benzoylecgonine, Tropacocaine, and Ecgonine Yields of the Coca Leaf. A. W. K. DE JONG (*Indische Mercuur*, 1923, **46**, 305).—The benzene extract of the leaves is evaporated, treated with 1% acetic acid, then with alcohol, and the residue redissolved in benzene from which the benzoylecgonine crystallises. Ecgonine is estimated in the remaining benzene solution by polarimetry. For the estimation of tropacocaine, the benzene extract is shaken with 0·1*N*-hydrochloric acid, which is titrated with 0·1*N*-sodium hydroxide. CHEMICAL ABSTRACTS.

Estimation of Procaine (Novocaine). ALFRED W. HANSON (*J. Assoc. Off. Agric. Chem.*, 1923, **7**, 17—20).—The bromide-bromate method described previously (A., 1922, ii, 405) is trustworthy, and the presence of small amounts of nitrates does not interfere. When the substance is extracted from its ammoniacal solution and titrated, the results obtained tend to be too low. W. P. S.

Detection of *apo*Morphine. L. VON ITALLIE (*Pharm. Weekblad*, 1923, **60**, 1046—1049).—The method of Feinberg (*Z. physiol. Chem.*, 1913, **84**, 363) is not always trustworthy. In a neutral solution, in presence of oxidising agents, red, violet, or blue colorations are imparted to organic solvents by traces of *apo*morphine after keeping. Ammonium persulphate, after addition of pure sodium hydrogen carbonate, gives a strong reaction with one part of *apo*morphine in 100,000 parts. S. I. L.

Improved Method for the Estimation of Nicotine in Tobacco and Tobacco Extracts. O. M. SHEDD (*J. Agric. Res.*, 1923, **24**, 961—970).—One g. of tobacco extract (more if much

lower than 40% grade) or 5 g. of dried and powdered tobacco are moistened with 2·5 c.c. of alcoholic sodium hydroxide solution ($NaOH$, 6 g.; water, 40 c.c.; 90% lcohol, 60 c.c.) For extracts twice this quantity is used, and enough calcium carbonate is added to make the whole into a moist mass. The mixture is extracted for five hours in a Soxhlet extractor with ether. The cooling water of the condenser should not be above 20° and the volume of solvent in the extraction flask should not be allowed to become less than 25 c.c. After extraction, excess of ether is removed, but the residual volume must not go below the minimum necessary to keep all extracted matter in solution. The ether extract is transferred to a separating funnel (washing out the flask first with ether and then with dilute hydrochloric acid) and washed with 4—6 portions (10 c.c. each) of cold dilute hydrochloric acid (1 : 4). A tendency to the formation of emulsions can be prevented by the addition of 1 c.c. of alcohol. Successive washings are filtered through glass wool into a 100 c.c. graduated flask. Washing with acid should be continued until no precipitate with the silicotungstic reagent is produced. The accumulated washings are made up to a standard volume, and an aliquot portion corresponding with about 0·25 g. of extract or 1—2 g. of tobacco, removed and diluted with water to 400—500 c.c. Sufficient hydrochloric acid (1 : 4) is added to ensure the presence of at least 3 c.c. per 100 c.c. of liquid. One c.c. of silicotungstic acid reagent (12% of the acid

$$4H_2O,SiO_2,12WO_3,22H_2O$$

—others are useless) is added for each 0·01 g. of nicotine presumed to be present. The mixture is stirred thoroughly until the crystalline precipitate will settle rapidly. A few drops of the supernatant liquid are tested to ensure that excess of the reagent has been added. After eighteen to twenty-four hours the precipitate is filtered, preferably through a Hirsch or Buchner funnel, and washed with dilute hydrochloric acid (1 : 1000), dried, and transferred without removal from the filter-paper to a platinum crucible. The latter is heated until all carbon is eliminated and finally ignited over a Teclu or Meker burner for not more than ten minutes. The weight of precipitate × 0·114 gives the weight of nicotine.

A. G. P.

[Analysis of] Potatoes with a High Content of Solanine. A. Bömer and H. Mattis (*Z. Unters. Nahr. Genussm.*, 1923, **45**, 288—291).—Solanine was estimated in potatoes by a variation of von Morgenstern's method, in which the extracted juice was made alkaline with ammonia, evaporated to dryness with 10 g. of kieselguhr, and extracted for five hours in Soxhlet's apparatus with 95% alcohol. The alcohol was evaporated off and the residue twice precipitated from warm dilute acetic acid solution with ammonia. The colourless product was weighed. The results obtained by this method were in some cases even higher than those given for the impure product of Schmiedeberg and Meyer's method, and were nearly twice those given by von Morgenstern's method for the same samples. They varied from 25·3 to 58·8 mg. per

100 g. for some samples of potatoes which were inedible, the values for normal potatoes being 2·0—7·5 mg. per 100 g. H. C. R.

Estimation of Pyramidone. ALFRED W. HANSON (*J. Assoc. Off. Agric. Chem.*, 1923, 7, 29—32).—Pyramidone may be extracted from its alkaline solution by chloroform, the extract then evaporated, the residue dried, and weighed. If desired, this residue may be converted into the hydrochloride, by evaporation with hydrochloric acid, and weighed as such, or the solution of the hydrochloride may be treated with silver nitrate solution and the silver chloride collected and weighed. The weight of silver chloride found is multiplied by 1·6131 to obtain the amount of pyramidone present. W. P. S.

The Estimation of Santonin in Flores Cinae (Tansy). L. M VAN DEN BERG (*Pharm. Weekblad*, 1923, **60**, 858—870).—After close examination of the methods of Katz (*Arch. Pharm.*, 1899, [*B*], 237) and others, a procedure was worked out, based on treatment of the hot aqueous suspension with dilute hydrochloric acid, extraction with chloroform, and recrystallisation from hot dilute alcohol. The santonin separated is not always pure, resin being usually present, especially when the santonin content of the powder is low. S. I. L.

Estimation of Methylene-blue. H. O. MORAW (*J. Assoc. Off. Agric. Chem.*, 1923, 7, 20—29).—In the iodometric method described, 0·1 g. of the methylene-blue is dissolved in 100 c.c. of water, the solution is treated with 30 c.c. of glacial acetic acid, and 30 c.c. of *N*/5-iodine solution are added. After fifty minutes, the mixture is diluted with water to 200 c.c., filtered, and the excess of iodine is titrated in an aliquot portion of the filtrate. Each c.c. of *N*/10-iodine solution is equivalent to 0·007475 g. of methylene-blue. W. P. S.

Fluorescent Oxidation Products of Bilirubin and their Importance as Sources of Error in the Detection of Urobilin. H. K. BARRENSCHEEN and O. WELTMANN (*Biochem. Z.*, 1923, **140**, 273—278).—The commonly employed method of detecting urobilin by oxidation to a green fluorescent substance with iodine in the presence of zinc acetate does not give trustworthy results when applied to body fluids other than urine. The complications are ascribed to the presence of bilirubin. J. P.

Arsphenamine [Salvarsan]. I. A Colorimetric Method for the Estimation of Salvarsan in Blood and Tissues. A. C. KOLLS and J. B. YOUMANS (*Bull. Johns Hopkins Hosp.*, 1923, **34**, 149—151).—A colorimetric method for the estimation of salvarsan is based on the diazotisation of the amino-groups, and the coupling of the diazotised product with orcin to produce a bright red substance. Details are given for the application of the method to whole blood, tissues, spinal fluid, blood plasma, and urine.

CHEMICAL ABSTRACTS.

General and Physical Chemistry.

Improved Temperature Control for the Pulfrich Refractometer. T. M. LOWRY and R. G. PARKER (*J. Sci. Instrum.*, 1923, **1**, 16—21).—Particulars are given of tests of a Pulfrich refractometer in which the temperature control is improved by the provision of water passages of greater bore than usual, the avoidance of unnecessary lengths of tube of small bore in the flow system, and the use of an additional water-jacket surrounding on three sides the liquid under examination. J. S. G. T.

Volume of the Molecule and Refractive Index. RICHARD LORENZ and W. HERZ (*Z. anorg. Chem.*, 1923, **127**, 205—208, 369—371; cf. A., 1922, ii, 821).—The quotient, ψ, of molecular refractive power, $[R_L]$, by molecular volume for all substances should be $\psi_s=0{\cdot}331$ at the boiling point, and $\psi_0=0{\cdot}4668$ at absolute zero (calculated according to the law of corresponding states). These values are quoted for some thirty compounds, and are found to deviate more or less from the theoretical. If $(n^2-1)/(n^2+2)$ really represents the volume of the molecules of a medium of refractive index n, then there should be some correspondence between $[R_L]$ observed and that calculated from the known radius of the molecule and the Avogadro number. Satisfactory agreement between these values is obtained in the case of carbon dioxide, hydrogen, methyl chloride, and ethylene.

ψ_s should be calculable not only from n_s, the refractive index at the boiling point, but also from D_s, the dielectric constant at the boiling point. Calculated in this way, ψ_s approaches more nearly to 0·331, the theoretical value, except in the case of dipolar molecules, which must show anomalous dispersion. H. H.

Contraction of Volume and Refractive Index of Liquid Mixtures. L. COUNSON (*Arch. Sci. phys. nat.*, 1923, **128**, 361—369).—The author has determined the respective densities and refractive indices, at about 20°, of aqueous solutions of tartaric acid and ammonium heptamolybdate containing either 10 or 25 g. per litre, and of mixtures of these solutions. The results indicate that q and c in Pulfrich's relation $(R-R_v)/R=q(D-D_v)/D=qc$, in which D and R are, respectively, the actual values of the density and refractive index of the mixture, whilst D_v and R_v are the corresponding values calculated on the assumption that these properties are additive in nature (Pulfrich, *Z. physikal. Chem.*, 1889, **4**, 561), are of the same sign (positive). J. S. G. T.

Disposition of an Arc in a Vacuum permitting the Obtaining of Spectra of Metals using Very Small Quantities of Material. (MLLE) BERTHE PERRETTE (*Compt. rend.*, 1923, **177**, 876—879).—The original paper should be consulted for details (including a diagram of the apparatus used). The cathode, of tungsten (or tungsten-thorium),

is maintained at a high temperature by an auxiliary current. The anode, a small disk of tungsten, contains a minute cavity in which the experimental material is placed. E. E. T.

Röntgen Spectrograph for Analytical Chemical Purposes. PAUL GÜNTHER and IWAN STRANSKI (*Z. physikal. Chem.*, 1923, **106**, 433—441).—A description is given of an *X*-ray spectrograph, and its use for chemical purposes is illustrated by measurements with a mixture of the rare earths from monazite from which cerium and thorium have been removed. J. F. S.

The Dependence of the Intensity of Spectral Lines on Gas Pressure. L. STRUM (*Z. Physik*, 1923, **18**, 372—378).—By application of the theory of probability to electronic orbits in their relation to the fields due to neighbouring atoms, an expression for the energy, E, emitted in the form of radiation of wave-length λ, by a gas at pressure p, through which a discharge passes, is deduced in the form $E=\delta pe^{-\gamma n^4 p^{2/3}}/\lambda$, where n is the appropriate quantum number associated with the line in the series formula, and δ and γ, are factors of proportionality. The formula is in accord with experimental results, more especially with the results obtained by Beatty (*Phil. Mag.*, 1917, [vi], **33**, 49; 1923, **45**, 1080) which indicate a maximum intensity of the line $H\alpha$ when the gas pressure is 1·4 mm. J. S. G. T.

The Multilinear Spectrum of Hydrogen. II. With an Addendum on the Continuous Spectrum. E. GEHRCKE and E. LAU (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1923, **24**, 242—252).—In continuation of previous work (this vol., ii, 197), the authors describe an arrangement suitable for the excitation of the red and green Fulcher bands of the hydrogen spectrum. They find that, in contradistinction to other lines in the multilinear spectrum, these bands are more strongly excited by slow cathode rays than by fast rays. Wave-lengths of lines constituting the red, green, and blue bands are detailed, and the potentials necessary for their excitation and the relative intensities of lines in the respective bands discussed. Residual lines in the bands are classified in three groups, one of which forms an approximately symmetrical series having its centre at λ 9799·25, whilst the remaining two groups exhibit an approximately constant difference between corresponding members of the respective groups. The conditions of excitation of the continuous spectrum between $\lambda\lambda$ 360 and $230\mu\mu$ resemble those for the excitation of the multilinear spectra. The possible origins of both these spectra are briefly discussed. J. S. G. T.

Excitation of the Spectra of Hydrogen and of Nitrogen in Low Voltage Arcs. O. S. DUFFENDACK (*Physical Rev.*, 1922, **20**, 100).—The fact that in a two-element tube the lines and bands of hydrogen appeared with the arc, whereas the bands did not appear when the gas was dissociated in the tungsten furnace, is additional evidence that the lines are due to the atom and the bands to the molecule. In the case of nitrogen, both the first and second positive bands appeared with the arc; the former increased, and

the latter decreased in intensity with increased voltage. The negative bands appeared one or two volts above the ionising potential, and increased markedly in intensity. Three new bands were observed at 5075, 5018, and 4961 Å. Four lines were observed at 5003, 5006, 5667, and 5680 Å., but never below 70 volts; at potentials above this, the arc became a "flare" with greatly increased conductivity. It is concluded tht the positive bands are due to the neutral molecule, the negative bands to the ionised molecule, and the lines to the atom, and that the molecule is ionised without dissociation. A. A. E.

The Distribution of Intensity in the Broadened Balmer Lines of Hydrogen. E. O. HULBERT (*Physical Rev.*, 1923, **22**, 24—36).—The broadening of the Balmer lines of hydrogen by condensed discharges was examined at various pressures, and the effect is ascribed to the large proportion of ionised atoms produced by the momentarily high current density. A. A. E.

The Effect of Crossed Electric and Magnetic Fields on the Hydrogen Spectrum. OTTO HALPERN (*Z. Physik*, 1923, **18**, 287—303).—The author develops a mathematical analysis showing how, by appropriate choice of variables, the Hamilton function associated with a hydrogen or singly-ionised helium atom in crossed electric and magnetic fields (combined Stark and Zeeman effects) may be expressed in the form of a convergent series capable of being quantised. It follows that, under such conditions, the hydrogen lines are split into a number of sharply defined lines and are not merely widened. J. S. G. T.

The Electron-affinity Spectrum of the Iodine Atom. WALTER GERLACH and FRITZ GROMANN (*Z. Physik*, 1923, **18**, 239—248).—According to Franck (*ibid.*, 1921, **5**, 428), the combination of an electron with an electrically neutral, electronegative atom should give rise to the emission of a continuous spectrum having a limiting frequency, ν_0, towards the red end equal to E/h, where E denotes the electron-affinity of the atom and h is Planck's constant. The authors suggest the identification of the continuous spectrum $\lambda\lambda$ 3460—3340 Å. emitted by dissociated iodine vapour with this electron-affinity spectrum. The value of the electron affinity of the iodine atom, calculated from this result is $81{\cdot}8+0{\cdot}2$ cal. per g.-mol., in close agreement with the mean value of about 82, calculated from the lattice energy of sodium iodide and potassium iodide by Born's lattice theory and with the same result deduced from the ionisation potential of hydrogen iodide. Evidence was obtained that the spectrum in the region λ 4800 Å., observed by Steubing (A., 1921, ii, 361), could not be identified with the electron-affinity spectrum of iodine vapour. J. S. G. T.

The Spectrum of Fluorine. HENRY G. GALE (*Physical Rev.*, 1922, **19**, 530).—Fluorine was prepared by Smythe's method (A., 1922, ii, 99), and its spectrum observed through a fluorite window at atmospheric or reduced pressure, using copper electrodes tipped

with gold. Of fifty-two lines between λ 3470 and λ 7800, all except seven on the red side of λ 7400 are included in the tables of Exner and Haschek, Porlezza, Lunt, or Moissan. With a powerful spark, fifteen additional lines appear in the red and orange regions.

A. A. E.

New Spectra of Oxygen and Nitrogen in the Extreme Ultra-violet. J. J. HOPFIELD (*Physical Rev.*, 1922, **19**, 548).—By the use of a disruptive discharge at low pressure, the spectrum of oxygen has been extended to include lines between λ 508 and λ 1335. Nitrogen, examined in a discharge tube of the internal capillary type, gave a spectrum extending from λ 825 to λ 1400, lines at λ 307 and λ 362 being also photographed. The spectrum of air was obtained with the same tube at a pressure of 3 mm., with two minutes' exposure, to λ 1050. A. A. E.

The Vacuum Spark Spectrum of Silicon. R. A. SAWYER and R. F. PATON (*Physical Rev.*, 1922, **19**, 256—257).—Previous investigations on the spark spectrum of silicon have exhibited but little agreement, largely on account of the rapid oxidation of the element. Application of the vacuum spark method has resulted in the observation of fifty-five lines between λ 4085·25 and λ 6372·2 to an accuracy of ±0·3 Å., those in the range 4100—5202 being probably correct to ±0·1 Å. Several groups of pairs of constant frequency difference have been noticed and tabulated. A. A. E.

Intensities in the Helium Spectrum. A. LL. HUGHES and P. LOWE (*Proc. Roy. Soc.*, 1923, [*A*], **104**, 480—498).—The authors have investigated the dependence of the distribution of intensities in the helium spectrum, excited by impacts between electrons and atoms, on the energy of impact of the electrons, which ranged from 34 volts to 210 volts, whilst all other factors were maintained constant. The results indicate that the curve expressing the relation of the intensity of any spectrum line to the corresponding energy of impact is characteristic of the series to which the line belongs. In the doublet system, intensities decrease rapidly as the energy of impact is increased above 34 volts. The rate of decrease is greatest for the sharp series $1\pi - m\sigma$, and least for the diffuse series $1\pi - m\delta$. The principal series $1S - mP$ of the singlet system is characterised by a very great increase of intensity as the energy of impact is increased from 34 volts up to about 80 volts, beyond which little change occurs. Maximum intensity of the lines of the diffuse series $1P - mD$ corresponds with an energy of impact of about 75 volts, the rise to the maximum being progressively greater the higher the term number associated with the line. Lines of the sharp series $1P - mS$ exhibit a small initial increase of intensity as the energy of impact is increased to 60 volts, and thereafter show a slight decrease. The results are discussed in the light of the quantum theory, and the authors conclude that the transitions from one energy level to another within an atom struck by an electron, are to some extent affected by the presence of other atoms, ions, or electrons. J. S. G. T.

The Spectrum of Neutral Helium. C. V. RAMAN and A. S. GANESAN (*Astrophys. J.*, 1923, **57**, 243—247).—The ionising potential computed from Silberstein's formula $\nu=4N(1/n_1^2-1/m_1^2+1/n_2^2-1/m_2^2)$ is not in agreement with the experimental value. Moreover, there is no arrangement of lines as regards series relationship, division into singlet and doublet systems, or of intensities. A. A. E.

The Spectrum of Helium. LUDWIK SILBERSTEIN (*Astrophys. J.*, 1923, **57**, 248—250; cf. preceding abstract).—The author's formula covers twenty-three of the thirty so-called combination lines; the probability that the coincidences of the computed with the experimental values is fortuitous is stated to be of the order 10^{-13}. A. A. E.

Measurements of Wave-lengths in the Visible Spectrum of Helium, and the Interference Phenomena Employed in the Measurements. (MLLE) H. C. OFFERHAUS (*Arch. Néerland.*, 1923, **7**, 60—94).—Details are given of the application of an étalon spectrograph, calibrated by means of the cadmium line λ 6438·4696 Å., to determine the wave-lengths of nineteen lines in the helium spectrum between λλ 3888·650 and 7281·348 Å. Results are recorded to 0·001 Å., and agree very closely with corresponding results obtained by Merrill (A., 1917, ii, 434). J. S. G. T.

Positive Ray Analysis of Lithium, Zinc, and Calcium. A. J. DEMPSTER (*Physical Rev.*, 1922, **19**, 271, 431; cf. A., 1922, ii, 417).—Positively charged atoms are formed by vaporising the metal in an electrically heated capsule, and bombarding the vapour with electrons from a hot cathode. After falling through a definite potential, the particles are deflected through 180° by a magnetic field, the semicircular path being smaller for the lighter than for the heavier particles. The different atoms are observed by means of their charge. The components of lithium have atomic weights 6 and 7 present in varying proportions. Zinc isotopes of atomic weights 64, 66, 68, and 70 exhibit large variations in their relative proportions. The zinc lines were compared directly with those of calcium, of which the strong line at 40 was compared with a potassium line at 39 and a magnesium line at 24; a weak calcium component has atomic weight 44. A. A. E.

Vacuum Grating Spectrograph and the Zinc Spectrum. R. W. WOOD (*Phil. Mag.*, 1923, [vi], **46**, 741—750).—The construction and operation of a vacuum grating spectrograph, with which lines of short wave-length may be photographed with extreme sharpness, are briefly described. The grating employed is of 1 metre radius and is ruled with 15,000 lines to the inch, the ruled surface measuring 1×4 inches. The source of light used is the electron-arc (*Physical Rev.*; 1897), and a full exposure of the Schumann plates employed requires about twenty minutes. The sharpness of lines in the zinc spectrum photographed with this instrument is compared with that of corresponding lines given by Sawyer (A., 1921, ii, 363). Wave-lengths and intensities of twenty-one lines in the zinc spectrum between

λλ 1601·15 and 1918·67 Å. and of forty lines between λλ 832·73 and 1307·32 Å. are tabulated and compared with values given by Sawyer. The values of wave-length determined are considered to be correct to 0·1 Å. Between λλ 1283 and 1500 Å., the author records 96 lines, compared with 14 given by Sawyer. No trace is found of ten lines recorded by the latter observer between λλ 1066 and 1165 Å. The carbon line 1036·1 Å. given by Sawyer is resolved into a clearly separated doublet λλ 1037·14 and 1037·50 Å. The carbon triplet, λλ 1561·32, 1560·67, 1560·16, resolved by Simeon (this vol., ii, 45), is considered to be a doublet with components of equal intensities and a separation of one Ångström unit. J. S. G. T.

Stages in the Excitation of the Spectra of Thallium. F. L. Mohler and Arthur E. Ruark (*J. Opt. Soc. Amer.*, 1923, **7**, 819—829).—In continuation of previous work (A., 1919, ii, 42; this vol., ii, 605), determinations have been made of the critical potentials, and the development of the spectrum with increasing voltage, in the case of thallium vapour. The first resonance potential has the value 0·9 volt, and the first ionisation potential the value 6·04 volts. The agreement between the latter value and the value, 6·082 volts, calculated for the level of greatest negative energy, confirms the view that $2p_2$ is a normal orbit of the atom. A higher critical potential, detectable by the photoelectric effect of the radiation, has the value 12·4 volts. With increasing voltage below the ionisation potential, successive lines of the two subordinate series in the thallium spectrum appear. Above 12 volts another line system, with strong lines in the ultra-violet, appears. It is suggested that this second spectrum is an arc spectrum resulting from a second type of single ionisation consisting in the removal of one of the two 6_1 electrons. Comparison of the critical potentials with the doublet series system of thallium indicates that the first ionisation potential is determined by the limit $2p_2$ and the first resonance potential by the difference $2p_2-2p_1$. The orbit $2p_1$ is meta-stable. Resonance potentials corresponding with frequencies $2p_2-ms$ and $2p_2-md$ give rise to the observed low voltage spectra. Corresponding critical potentials are calculated for aluminium, gallium, and indium. J. S. G. T.

Two New Lines in the Aluminium Spectrum and their possible Series Relations. G. D. Shallenberger (*Physical Rev.*, 1922, **19**, 398—399).—The application to aluminium electrodes of a high potential vacuum spark yields strong, well-defined lines at λ 4150·6 and λ 2907·4 (±0·3—0·4 Å.), respectively. Equations are given representing the frequencies of the lines, which can scarcely be due to impurities; certain numerical relations are also mentioned. A. A. E.

Pole Effects, Pressure Shifts, and Measurements of Wave-lengths in the Spectrum of Manganese. George Spencer Monk (*Astrophys. J.*, 1923, **57**, 222—233).—Pole effects, pressure shifts, and wave-lengths for the stronger lines of manganese between λ 4470 and λ 6021 have been measured. The evidence indicates a

correspondence between unsymmetrical broadening of the lines under pressure and pole effect. The use of a carbon pole bored and filled with manganese dioxide or of manganese poles gave moderate pole effects which were practically absent when manganese chloride was used. The wave-lengths of forty-one lines have been measured with an estimated accuracy of 0·002 Å., and tabulated.

A. A. E.

The Intensity of Röntgen Spectral Lines Excited by High Voltages. GUSTAV KETTMANN (*Z. Physik*, 1923, **18**, 359—371).—A method for determining photographically the intensities of Röntgen spectral lines is described, and measurements of the relative intensities of lines, excited at various voltages, in the *K*-series of chromium, copper, and silver, and in the *L*-series of lanthanum and lead, are detailed. At high voltages, the intensities of the lines attain a maximum value, owing to absorption of the rays by the anti-cathode. When absorption of the rays by the anti-cathode is very small, the respective intensities of the lines increase proportionally to the square of the voltage. The results are found to be in agreement with the theory proposed by Davis (*Physical Rev.*, 1918, **11**, 433). J. S. G. T.

Spectra of Isotopes. A. L. NARAYAN (*Nature*, 1923, **112**, 651).—The structure of the tin lines 5631 and 4524 was carefully examined with a Lummer plate. Even when the pressure was of the order of 1 mm., both lines were simple in structure, the latter being especially sharp. McLennan's view (A., 1922, ii, 541, 728) that the spectral displacement for isotopes should be given by the atomic number multiplied by the displacement calculated on Bohr's theory, requiring in this case a difference for isotopes 116 and 124 of 0·07614, is therefore not supported. A. A. E.

The Optical Spectrum of Hafnium. H. M. HANSEN and S. WERNER (*Nature*, 1923, **112**, 618—619).—Both the arc and the spark spectra of hafnium have been investigated, using a preparation of hafnium containing (according to *X*-ray analysis) not more than about 1% of zirconium. The previous results (this vol., ii, 200) in the case of the arc spectrum have been confirmed and extended. Comparison of the results with those of Bardet (this vol., ii, 449) appears to indicate that the hafnium spectrum, like that of zirconium, differs according to the conditions of excitation. The wave-lengths between λ 2497·0 and 3505·2 and the intensities are tabulated. A. A. E.

***X*-Ray Spectra of Hafnium and Thulium.** D. COSTER (*Phil. Mag.*, 1923, [vi], **46**, 956—963).—Particulars are given of physical methods employed in the discovery and investigation of the properties of the element of atomic number 72. The following wave-lengths (measured in *X*-units) have been determined in the *L*-series of the emission spectrum of hafnium: 1777·4, 1577·04, 1566·07, 1519·7, 1389·3, 1371·1, 1349·7, 1323·5, 1303·5, 1212·1, 1176·5, 1141·3, 1135·6, 1100·1. The estimated error is in all cases less than 0·4 *X*-unit. In addition, the following lines in the *L*-series of the

absorption spectrum of hafnium were determined: 1097, 1151·5, 1293·0, and the following lines in the *M*-series: 7521, 7286. Values of the wave-lengths in the *L*-series of the spectrum of the element of atomic number 69 (thulium) have been determined as follows: 1951·1, 1733·9, 1722·8, 1692·3, 1541·2, 1526·8, 1511·5, 1502·3, 1460·2, 1352·3, 1312·7, 1271·2, 1265·3, 1226·4 *X*-units. The author discusses the identification of two *X*-ray lines found by Dauvillier in the spectrum of a preparation of rare-earth metals and ascribed to celtium, the presence of which was suspected by Urbain (A., 1922, ii, 463). J. S. G. T.

Critical Potentials of the Thorium *M*-Series Lines. P. A. Ross (*Physical Rev.*, 1923, [ii], 22, 221—225).—The lines, α to ϵ, of Stenström, and a new line, ϵ_2, of wave-length 2·85 Å., were observed. The critical potentials were found to agree with the predicted values. A. A. E.

Trithiocarbonic Acid and Perthiocarbonic Acid. H. von Halban, A. Mackert, and W. Ott (*Z. Elektrochem.*, 1923, 29, 445—457).—The absorption spectra of solutions of trithiocarbonic acid (H_2CS_3) and its ethyl ester have been obtained for solutions in chloroform, ethyl alcohol, light petroleum, ether, and toluene, and that of the barium salt in water. Similar measurements have been made with solutions of perthiocarbonic acid (H_2CS_4) in chloroform, toluene, and light petroleum, and the sodium salt has been measured in aqueous solution. Very large differences are found between the spectra of the acids and those of the salts. These differences are shown by changes in the colour, which are similar to those observed with indicators. The actual existence of the free acid is amply proved by the similarity of the absorption spectrum of a solution of the sodium salt with that obtained for a solution prepared by shaking an organic solution of the acid with sodium hydroxide. The absorption curves of the acids in various solvents differ relatively little from one another, and in no case are they similar to those of the salts. The curve for the ester is similar to that of the acid, but shows a considerable displacement, and in no case can the curve for the acid be made up from the curves for the salt and ester. The absorption spectra of ethyl-thiocarbonic acid in organic solvents and its potassium salt in water and alcohol solution have also been obtained. In this case also, a marked optical effect is observed on the formation of the salt. The introduction of the first and second ethyl groups into the trithiocarbonic acid molecule produces similar displacements of the absorption spectrum. *p*-Chloro- and *p*-bromobenzyl-trithiocarbonic acids have been prepared. These substances are solid and fairly stable. The absorption spectra of the chlorobenzyl acid and of its potassium salt have been obtained and show the same differences as those found in the case of the ethyl acid and its potassium salt. The chlorobenzyl acid has a normal molecular weight in benzene solution. The velocity of decomposition of trithiocarbonic acid, perthiocarbonic acid, ethyl-trithiocarbonic acid, and *p*-chlorobenzyl-trithiocarbonic acid has been determined in several organic solvents, and it is shown that the influence of the solvent

on the decomposition is generally the same as in the case of the xanthic acids (A., 1913, ii, 312; 1918, ii, 222). The behaviour of the *p*-chloro- and *p*-bromo-benzyl acids towards the diazo-esters depends on the solvent in a way which is entirely different from that found by Hantzsch for oxygen acids (this vol., ii, 475). J. F. S.

Colour of Inorganic Compounds. W. BILTZ (*Z. anorg. Chem.*, 1923, **127**, 169—186, 372; cf. Meisenheimer, A., 1921, ii, 364). —An attempt to provide a theory of the colour and constitution of inorganic compounds. Unsaturation is shown to be the chief factor in determining such colour. "Mixed" compounds formed by the union of compounds of elements in different states of oxidation show a deeper colour than either of the parent compounds, whether the components contain the same element or not. Thus AuCl is bright yellow, and $AuCl_3$ is orange, whilst Au_2Cl_4 is nearly black. Similarly, ZnO and Al_2O_3 are both colourless, but ZnO,Al_2O_3 is violet. Magnetic power is also associated with colour—iron, cobalt, nickel, manganese, vanadium, copper, and chromium are all chromophores. Again, both "sub-" and "super-" compounds are coloured, and may be regarded as unsaturated. In the case of substances which contain elements of variable valency, it is found that the colour deepens as the valency decreases, if the normal valency is the highest, and conversely. Dissociation deepens colour because it increases unsaturation; and, in general, the stronger the linking between elements, the less the colour of the resulting compound. H. H.

Determination of Coefficients of Absorption. H. A. C. DENIER VAN DER GON (*Arch. Néerland.*, 1923, 7, 140—155).—Employing a thermopile and galvanometer to indicate the respective intensities of the incident and transmitted radiation, the author has determined the coefficients of absorption, at about 20°, of aqueous solutions of cupric chloride containing from 0·310 to 4·50 g.-mols. per litre, and of aqueous solutions of copper sulphate containing, respectively, 0·190 and 1·15 g.-mols. per litre, for radiation of wave-length from 411 $\mu\mu$ to 810 $\mu\mu$. The results indicate that in the case of the solutions of copper sulphate, Beer's law is approximately obeyed in the case of radiation of wave-length greater than 550 $\mu\mu$. A like result holds in the case of the solutions of cupric chloride for wave-lengths in the neighbourhood of 565 $\mu\mu$. In this region, the respective absorption curves, drawn by plotting the logarithm of the respective coefficients of absorption as ordinates against the corresponding wave-lengths as abscissæ, are coincident, whilst for radiation of greater wave-lengths, the curves differ only slightly. Absorption in these cases is attributable to the copper contained in the solutions. Each curve exhibits a well-marked minimum at a point corresponding with a shorter wave-length than that referred to. J. S. G. T.

Colour and Chemical Constitution. XVIII. Colourless Substances in Sulphuric Acid (Halochromy). JAMES MOIR (*Trans. Roy. Soc. S. Africa*, 1923, **11**, 91—93; cf. this vol., ii, 108).—A method has been discovered for predicting the colour produced

when certain colourless substances are dissolved in concentrated sulphuric acid (halochromy). The laws are apparently simpler than for aqueous solution, a single set of colour factors applying to all substances. The absorption is generally above λ 360. The absorption can be calculated from that of a parent substance (*p*-hydroxybenzyl alcohol) by multiplying by colour factors depending on the difference of the compound from the parent substance. The absorption of *p*-hydroxybenzyl alcohol is λ 488. The substitution factors are: phenyl for hydrogen 0·96; phthalein or $C_6H_4\cdot CO_2H$ for hydrogen, 1·01; hydroxyphenyl for hydrogen, 1·02; hydroxyphenyl for phenyl, 1·06; bridge oxygen, 0·87; hapton oxidation, *e.g.*, benzhydrol to benzophenone, 0·89 or 0·70. E. H. R.

The Colour of Monocyclic Substances Calculated by Assigning an Absorption Band to Each Possible Tautomeric Form. JAMES MOIR (T., 1923, **123**, 2792—2803.)

The Absorption Spectrum of Chloroform in the Near Ultra-red. J. W. ELLIS (*Physical Rev.*, 1922, **19**, 546).—Five distinct bands were observed with maxima at 1·140 μ, 1·385 μ, 1·660 μ, 1·835 μ, and 2·425 μ, the percentage of absorption being, respectively, 10, 16, 56, 35, and 88. The error may be ±100 Å. A. A. E.

The Ultra-violet Absorption of Anthracene and Benzene. J. M. HYATT (*Physical Rev.*, 1922, **19**, 391—393; cf. Howe, *ibid.*, 1916, **8**).—For a solution of anthracene in ethyl alcohol, fourteen bands having frequency numbers 2650, 2700, 2800, 2840, 2945, 2990, 3095, 3130, 3240, 3410, 3540, 3688, 3975, and 4115, respectively, were observed. The numbers fall into two series with mean frequency intervals of 147 and 142, respectively. For a solution of benzene in ethyl alcohol, ten bands were observed, as follows: 3720, 3780, 3830, 3920, 4015, 4120, 4210, 4295, 4365, 4465. A. A. E.

Radiochemistry and Fluorescence. JEAN PERRIN (*Compt. rend.*, 1923, **177**, 665—666; cf. this vol., ii, 714).—The thermal coefficient of the disappearance of new-methylene-blue in glycerol solution, in absence of air and under the influence of light, is 1·6 for temperatures between 19° and 81°, giving 9×10^{13} for the frequency of the infra-red rays which produce critical glycerol molecules. With constant illumination, for concentrations below 5%, the disappearance obeys the law of mass action at the above temperatures. That is, the concentration of critical mols. of dye is always proportional to the concentration of unactivated dye. New-methylene-blue disappears 1,200 times as rapidly as fluorescent-blue, the thermal coefficients, however, being the same. The second blue therefore reacts with the same kind of critical glycerol molecules, produced either by absorption of infra-red radiation or by equivalent intermolecular shocks. A previous deduction, that the direct action of a critical molecule (produced using external radiation) on a non-critical molecule should be unaffected by variations of temperature, is now proved for uranine and eosin (sodium salt), the disappearance-velocities of which are unaffected by temperature elevations of 60° and 90°, respectively. E. E. T.

The Luminescence of Solidifying Antimony. E. KARRER (*Physical Rev.*, 1922, **19**, 437—438).—When heated at a temperature above its melting point, antimony becomes bright red; on cooling, the brightness decreases with the temperature until solidification commences, when a sudden increase in brightness occurs, accompanied by an increase in temperature. Moreover, the brightness after the flash appears greater for a given temperature than the brightness at the same temperature before the flash. It thus appears to be a case of crystal-luminescence; the phenomenon is not due to oxidation of the antimony, since it takes place in hydrogen or in a vacuum. A. A. E.

Determinations of Structure in Conformity with the Electron Theory. C. J. ENKLAAR (*Rec. trav. chim.*, 1923, **42**, 1000—1016).—The author treats refractive dispersion from the point of view of valency electrons and considers that every atom in a saturated open-chain compound has the same number of dispersion electrons as it has valencies. Satisfactory agreement is found in many cases quoted. In benzenoid compounds, however, he finds that each carbon atom possesses twelve, instead of four, dispersion electrons, if it occurs in the nucleus, and, further, that the same is true of unsaturated carbon atoms in open-chain compounds. Determinations of the refractive dispersion of cyanogen lead to the adoption of the formula N⋮C·C⋮N for this compound. The theory is also applied to the determination of the structure of 1 : 3 : 5-trienes. H. H.

Mutarotation. II. C. N. RIIBER (*Ber.*, 1923, **56**, [*B*], 2185—2194).—In continuation of previous work (A., 1922, ii, 807), it is shown that the change in refractive index of aqueous solutions of dextrose when preserved takes place exactly parallel to the alteration in specific rotation and in accordance with the equation for a unimolecular reaction. The velocity constant and the half period is the same as that deduced from measurement of specific rotation or change in volume of the solution, and the three phenomena are therefore attributable to the same cause.

The equilibrium between α-glucose, β-glucose, and glucose hydrate in aqueous solution has been fully examined; solutions of any modification containing 10% of anhydrous substance are identical after twenty-four hours as judged by density (d_4^{20} 1·037881), specific rotation ($[\alpha]_D^{24}$ +52·1°), or refractive index (n_D^{20} 1·34778). If α- and β-glucose are actually in equilibrium in solution, it follows that the opposite physical changes must be observed on solution of the two varieties. This has been shown previously to be the case with the specific rotation, and is now found to be true for density, index of refraction, and heat of reaction. The actual establishment of an equilibrium is more firmly established by the observation that the half period of α-glucose is the same as that of β-glucose as determined by dilatometric, refractive, or polarimetric methods. Further, it is found that a solution of α-glucose (3·61 g.), and β-glucose (6·39 g.) in water (90 g.) does not change in density, refractive index, or specific rotation when preserved.

Glucose hydrate has frequently been considered to be an ortho-form of the true aldehyde, and not a hydrate in the usual sense. Trey's observation that solutions of glucose hydrate undergo contraction when preserved appears, however, to be erroneous, since a dilation takes place which is of the same magnitude as that observed with anhydrous glucose. Examination by the three methods has failed to disclose any difference between solutions of glucose and the hydrate which contain the same amount of anhydrous material and are of the same age. The author therefore draws the conclusion that there is no evidence of the existence of an appreciable amount of glucose hydrate or the ortho-form of glucose in aqueous solution, although the possibility is not excluded that it may be present in an amount too small to be detected by the physical methods employed, as is indicated by the behaviour of the solutions towards hydroxylamine and phenylhydrazine.

The opinion has been frequently expressed that mutarotation is impossible in the absence of a solvent. It is shown, however, that if dehydrated α-glucose is melted and cooled rapidly to the atmospheric temperature it has then an initial specific rotation of about 50° in water; the same result is observed when β-glucose is employed. Apparently, therefore, the fused masses are identical and consist (mainly) of an equilibrium mixture of the α- and β-forms. This is supported by the observation that the seeding of the under-cooled melt with α- or β-glucose induces the complete crystallisation of it as the α- or β-form, respectively, whereas a mixture of the two varieties is formed when a mixed seed is used.

Mutarotation, therefore, may be induced by melting an optically active substance, by bringing such a substance into solution, or by alteration in the concentration or temperature of the solution of the substance. H. W.

Magnetic and Natural Rotatory Dispersion in Absorbing Media. E. O. HULBERT (*Physical Rev.*, 1923, **22**, 180—187).—By a consideration of absorption of the radiation in a transparent medium, more complete formulæ for rotatory dispersion than those hitherto put forward have been derived. Certain approximations have been made, and simplified formulæ obtained which give the rotation for wave-lengths sufficiently removed from the critical wave-length, provided the refractive index and extinction coefficient conform to the Lorentz dispersion equations with one resonance frequency. In the case of carbon disulphide and 1-bromonaphthalene, the equation of magnetic rotation in isotropic media agrees closely with the experimental results. A. A. E.

Action of Red and Infra-red Radiations on Photo-luminescent Substances. MAURICE CURIE (*J. Chim. Phys.*, 1923, **20**, 292—307).—The action of red and infra-red radiation on photo-luminescent substances has been investigated in the case of zinc sulphide and calcium sulphide. In the case of zinc sulphide, it is shown that a black spot is formed on a background of brilliant luminescence at the point where the infra-red rays are concentrated. This fact indicates that these rays not only excite luminescence, but also

destroy it. When the sulphide is removed from the rays, a very brilliant luminescence is seen at one spot followed by a very dark band. This reinforcement of the luminescence varies in intensity and in the time of its duration with the nature of the phosphorescent substance. With zinc sulphide containing copper, the colour is green, and it is maintained for a much shorter time than with zinc sulphide containing manganese, in which case the colour is yellow. There are no resonance phenomena observable in the present experiments. J. F. S.

Darkening of Zinc Sulphide by Light. ARTHUR SCHLEEDE [with M. HERTER and W. KORDATZKI] (*Z. physikal. Chem.*, 1923, **106**, 386—398).—Zinc sulphide prepared in various ways has been examined in connexion with its darkening under the influence of light. It is shown that precipitated and non-ignited zinc sulphide does not darken under any conditions of illumination. Ignited zinc sulphide which is free from materials with which it has been heated, shows a sensitiveness towards light from a quartz mercury lamp when the temperature of ignition is so high that measurable quantities of wurzite are formed. The zinc blende form of zinc sulphide is not affected by ultra-violet light from a mercury lamp. The presence of small quantities of heavy metals makes no change in the action of light in these cases. Crystallised zinc sulphide containing halogen compounds is sensitive to the long wavelength ultra-violet light, and the presence of small quantities of heavy metals intensifies the action. The sensitiveness of halogen containing zinc sulphide can be removed by washing the material, so far as the long wave-length ultra-violet light is concerned, but this has no effect on short wave-length ultra-violet light effect or on the phosphorescence. Sensitiveness to long wave-length ultraviolet light is apparently induced by fusing zinc sulphide (wurzite) with a halogen salt. J. F. S.

Temperature Coefficient of Photochemical Reaction Rate. RICHARD C. TOLMAN (*J. Amer. Chem. Soc.*, 1923, **45**, 2285—2296). —A theoretical paper in which, on the basis of the quantum hypothesis, a simple equation for the temperature coefficient of photochemical reaction velocities has been derived. The equation agrees with that previously obtained (A., 1921, ii, 99) by the author using the methods of statistical mechanics. The existing data on temperature coefficients of photochemical reactions have been successfully interpreted with the help of the equation. It has been shown that Plotnikov's division of photochemical temperature coefficients into three distinct classes is apparently not tenable. An equation for change in temperature coefficient with frequency has been derived and used successfully in interpreting existing data. The causes of apparent deviations from Einstein's law of photochemical equivalence have been discussed. J. F. S.

Theory of Radiation Transformation. II. Photochemical Chlorine Reaction. FRITZ WEIGERT (*Z. physikal. Chem.*, 1923, **106**, 407—432; cf. this vol., ii, 3).—A theoretical paper in which

as an example of a photochemical chlorine reaction the decomposition of ozone in the presence of illuminated chlorine is discussed. The facts, that the velocity of the reaction is independent of the ozone concentration and that, according to Bodenstein and Bonhoeffer (*Z. Physik*, 1923, **13**, 94), it takes place in accordance with the quanta of light energy absorbed by the chlorine, show that an upper limit of the concentration of ozone exists at which the whole of the light energy absorbed by the chlorine is converted into chemical energy. The same case is found in the sensitisation of the hydrogen dissociation for the resonance lines of mercury by dilute mercury vapour. In this case, with a limiting pressure of hydrogen, practically the whole of the absorbed resonance energy is converted into chemical energy. The limiting pressures of the reacting molecular species, ozone 0·5 mm. and hydrogen 10 mm. of mercury, and their relationship to the pressure of the sensitising molecules (chlorine ½ atm., mercury 0·009 mm.) are widely different. The quantity relationship n_r/n_s in the case of the chlorine–ozone reaction is $1 \cdot 3 \times 10^{-3}$, and for the hydrogen–mercury reaction $1 \cdot 1 \times 10^3$. If, on the other hand, the number of molecules is calculated in layers which produce the same amount of weakening of the radiation, they will be found to be the same in the two reactions. It is therefore likely that in both processes the initial stage is the same. The hypothesis is advanced that the radiation absorbed by the excited molecules is at first re-emitted as resonance radiation in the normal manner, and that this absorption and emission process is repeated so often that at last the absorption leads, in a binary absorption system, to an internal photoelectric effect, whereon a chemical process or a translatory displacement of the particles follows. Whereas the resonance radiation with mercury, on account of the extremely strong absorption of the mercury vapour for the exciting resonance line, is easily observed, this can scarcely be expected in the case of chlorine with its hundred million times smaller absorption constant. But there are indirect reasons for the non-thermal absorption of pure chlorine. The thermal increase in volume during radiation is only to be observed in the presence of moisture or other impurities. According to this view, the transformation of absorbed energy to the chemical reacting system does not occur simultaneously with the absorption of the radiation; the process requires, on account of the repeated absorption and emission of a once absorbed energy quantum, a definite time before it is completed. The energy quantum remains, in a sense, in the reacting system until it is entirely used up. The measurement of such short retardations can be carried out by the new Weigert and Kellermann method (A., 1922, ii, 808). The application of this method to the photochemical chlorine–hydrogen reaction has shown a retardation of about 1/100 sec. It is, however, not certain that this measured delay is due to the above effect, since the yield in this reaction is much larger than Einstein's law demands. The delay can also be explained by assuming a long chain of reactions. Many such mechanisms have been put forward which are discussed. A special photoelectric effect is assumed, which may represent the primary

process by which the chlorine-hydrogen reaction is started. This assumption does away with the necessity of assuming excited chlorine molecules and a splitting of the molecules into atoms. It may be concluded that ozone will be decomposed by long wave-length ultra-violet radiation in the absence of any other substance, and that perhaps the radiation absorbed by the chlorine falls in the ozone absorption band and that during the repeated absorption and re-emission it is used up in this weak absorption region.

J. F. S.

The Photochemical Reactivity of Ozone in presence of Other Gases. I. ROBERT OWEN GRIFFITH and WILLIAM JAMES SHUTT (T., 1923, **123**, 2752—2767).

The Photochemical Reactivity of Ozone in presence of Other Gases. II. ROBERT OWEN GRIFFITH and JANE MAC-WILLIE (T., 1923, **123**, 2767—2774).

Decomposition of Ammonia by Ultra-violet Rays, and the Law of Photochemical Equivalence. W. KUHN (*Compt. rend.*, 1923, **177**, 956—957).—The decomposition of ammonia, prepared by heating its silver chloride derivative, has been studied in quartz vessels, monochromatic light of known wave-length (from 2025—2140) being used as the source of energy. (In complete light, the decomposition proceeds to completion, at a speed proportional to the energy absorbed. Aqueous solutions of the gas undergo no decomposition under similar conditions.) The number of quanta absorbed by 1 mol. of ammonia, undergoing decomposition, varies from 2—2·5, and is independent of the pressure (900—5 mm.). For temperatures of 10—20°, the speed of decomposition is independent of *t*, and, generally, this speed is not affected by the size of the quartz surfaces (whereas the thermal dissociation is accelerated by quartz surfaces). The speed of decomposition is also unaffected by the addition of metallic sodium, and is therefore independent of the action of minute traces of water. With monochromatic light of $\lambda = 2063$, the number of quanta necessary to decompose 1 mol. of ammonia is 3·4, or as many as 10 if the monochromatisation is very perfect. From the heats of dissociation for $N_2 = N + N(-140{,}000$ cal.), $H_2 = H + H(-84{,}000$ cal.), and $NH_3 = 0{\cdot}5N_2 + 1{\cdot}5H_2(-11{,}000$ cal.), whence $NH_3 = N + H_2 + H - 123{,}000$ cal., and $NH_3 = N + H + H + H - 207{,}000$ cal., it follows that a quantum $h\nu$ for the ray 2063 corresponds with 128,000 cal. per g.-mol. The energy furnished by the absorption of a quantum suffices for the first, but not for the second change. On these lines may be explained the facts that several quanta are required to decompose 1 mol. of ammonia, and that the speed of decomposition depends on the perfectness of monochromatisation of the ultra-violet radiation.

E. E. T.

The Photochemical Decomposition of Silver Bromide. II. ROBERT SCHWARZ and HEINRICH STOCK (*Z. anorg. Chem.*, 1923, **129**, 41—54; cf. A., 1921, ii, 614).—Attempts were made to find the relationship between the age and the photochemical decom-

position of silver bromide, using the mercury lamp as a source of light. Very irregular curves were obtained, however, the irregularities being ascribed to (1) moisture, the loss of which decreased the rate of separation of bromine, and (2) grain size, which increased with age. Colloidal sols act as catalysts; silica is a positive and platinum, zirconium hydroxide, stannic acid, and gelatin negative catalysts. W. T.

The Formation of Organic Compounds from Inorganic by the Influence of Light. OSKAR BAUDISCH (*Science*, 1923, 57, 451—456).—The observation that cholera bacilli rapidly reduce nitrates to nitrites, the velocity of the reaction being dependent on the bacterial iron content, led to a study of the catalytic effect of iron in the reduction of nitrates and nitrites. Dextrose in alkaline solution reduces nitrites, but not nitrates, and then only in the presence of traces of iron. Ferrous hydrogen carbonate or hydroxide does not reduce alkali nitrates even at 100° in the absence of oxygen; the presence of oxygen, however, causes immediate reduction to nitrite, and there is a direct relation between the amount of oxygen dissolved in the water and the amount of nitrite formed. This "fertilisation" process involves the production of a peroxidic iron compound, nitrite, and the reactive intermediate substance potassium nitrosyl, KNO. The latter substance reacts with aldehydes with the formation of hydroxamic acids, OH·CR:N·OH. It is considered that the magnetic properties of the peroxide are in direct relation to its great chemical activity. The action of potassium pentacyanoperoxoferroate, $K_3[FeO_2(NC)_5]$ in behaving as an oxygen carrier and activator is likened to a simple type of respiration. Whilst light of long wave-length brings about the formation of an alkaline aquo-base from potassium ferrocyanide solution, the reduction of alkali nitrates is effected only by light of short wave-length. In summer sunlight, alkali nitrates can be reduced to nitrite in a short time if small quantities of complex salts, *e.g.*, potassium ferrocyanide, are present. Formaldoxime and formaldehyde in sunlight form cyclic nitrogen compounds which contain pyridine and pyrrole rings and give the typical alkaloidal reactions. An aqueous solution of acetaldoxime and formaldehyde when exposed to sunlight gives a thick, dark brown syrup which has not been investigated. Nitromethane also unites with formaldehyde under the influence of light, or in weakly alkaline solution, *iso*-nitrobutylglycerol being formed intermediately. The author's observations of the formation of formhydroxamic acid, methylamine, alkaloids, and α-amino-acids have been confirmed and extended by Baly. Illumination of alkali nitrates with daylight in the presence of formaldehyde yields gases agreeing qualitatively with those formed by soil bacteria, and (in the presence of iron salts) formhydroxamic acid and formaldoxime. It is thought possible that many soil bacteria and also green leaves utilise nitrous oxide from the air for nitrogen nutrition. Although at considerable altitudes, or by the influence of silent electric discharges, carbon dioxide can be reduced to formaldehyde, which may then react

with nitrous oxide from atmospheric nitrogen and oxygen to yield formhydroxamic acid, it is not thought possible that the reduction can be effected by sunlight at sea level without the aid of chlorophyll. A. A. E.

Relation between the Energies of Alpha-particles and the Atomic Numbers of the Elements. L. MYSSOWSKY (*Z. Physik*, 1923, **18**, 304—306).—It is shown that the great majority of the radioactive elements can be arranged on four parallel and equidistant straight lines, drawn so that abscissæ represent atomic numbers, and ordinates the respective kinetic energies of the α-particles emitted from the elements. The position of thorium is uncertain. Thorium-*C*, actinium-*C*, uranium-*II*, and radium-*C* do not lie on the straight lines, and it is pointed out that at these elements the radioactive series branch. J. S. G. T.

Cathode-ray Furnace. HANS GERDIEN and HANS RIEGGER (*Wiss. Veröffentl. Siemens-Konzern*, 1923, **3**, 226—230).—A cathode-ray furnace, employing an exhausted spherical glass flask of diameter up to 50 cm., silvered externally or surrounded by acidified water, and provided with a cylindrical neck is described. Cathode rays emitted normally from the external electrode described impinge radially on the material to be heated, supported at the centre of the sphere on a rod passing axially through the neck of the flask. The use of an external electrode permits the furnace being operated with high-tension high-frequency current.

J. S. G. T.

Cathodoluminescence of Heated Alumina. D. T. WILBER (*Physical Rev.*, 1922, **20**, 101).—Ordinary powdered alumina, built up into a fritted cone, when freshly prepared shows coloured bands under cathode rays. The component ruby, green, blue, and orange bands appear in areas within restricted temperature limits. The ruby bands are due to the presence of minute traces of chromium. A mixture of alumina and magnesia in molecular proportions with 1% of manganese gave a brilliant green band; alumina and lime with manganese as active metal gave a broad band in the yellow and green. Alumina and lime with copper gave a band in the blue.

A. A. E.

The Excitation of Characteristic *X*-Rays from certain Metals. FRANK HORTON, URSULA ANDREWES, and ANN CATHERINE DAVIES (*Phil. Mag.*, 1923, [vi], **46**, 721—741).—The authors have investigated the voltages connected with some of the longer wavelength *X*-ray absorption limits in the case of the elements aluminium, iron, nickel, copper, and zinc, employing for this purpose the excitation potential method (cf. Kurth, A., 1922, ii, 410). The following respective critical values of the potential (expressed in volts) were determined: aluminium, 42, 66, and 107; iron, 73 and 166; nickel, 104 and 178; copper, 112 and 193; zinc, 119 and 200. By extrapolating the Moseley curves for the various absorption limits to low atomic numbers, it was found that the lower and higher values determined in the cases of the metals iron, nickel, copper, and zinc

were respectively associated with $M^{II, III}$ and M^{I} levels. The changes in the slopes of the M^{I} and $M^{II, III}$ curves in passing through the observed points support the view that a change in the constitution of the M electronic group occurs during the passage from one of these elements to another. Likewise, the results indicate that the development of the second M sub-group from four electrons to six electrons does not commence before the element cobalt (atomic number 27), and that the similar development of the first M sub-group commences at a lower value of the atomic number. By similar extrapolation of the Moseley curves for the L absorption, it was found that the critical potentials 66 volts and 107 volts found in the case of aluminium are respectively associated with the $L^{II, III}$ and L^{I} levels. From analogy with the anomalous K absorption limits found by Fricke for titanium, vanadium, and chromium (A., 1921, ii, 6), it is probable that the value, 42 volts, found for aluminium is associated with the displacement of an electron from the second L sub-group to the first M sub-group.

J. S. G. T.

Luminescence Produced by Röntgen Rays. A. Jaubert de Beaujeu (*J. Phys. Radium*, 1923, 4, 257—267).—Particulars are given of the principal wave-lengths and relative intensities of the fluorescence excited in various solid solutions of the rare earths, and in a large number of organic solid substances, by the incidence of Röntgen rays. Amongst the latter substances, aromatic compounds exhibit the phenomenon most markedly, and it is suggested that, in these cases, fluorescence is attributable to the presence of the benzene ring.

J. S. G. T.

The Secondary Corpuscular Rays produced by Homogeneous X-Rays. H. Robinson (*Proc. Roy. Soc.*, 1923, [*A*], **104**, 455—479).—In continuation of previous work (A., 1914, ii, 696), the author has investigated the "line spectra" of the secondary corpuscular radiation emitted from targets of bismuth, lead, gold, tungsten (metal and WO_2), barium ($BaCO_3$), iodine (LiI and AgI), tin, silver (metal and AgI), molybdenum, strontium ($SrCO_3$), copper, and various light atoms, including calcium, potassium, sulphur, magnesium, sodium, and oxygen, by the incidence of X-rays corresponding with the copper $K\alpha_1$ radiation. The various measurements are considered to be correct to within 1 part in 1000 parts. In general, the respective values of the energy levels of the emitted radiations agree very closely with those tabulated by Bohr and Coster. The apparatus enabled the three limits of L-radiation to be determined as far down as strontium (38). Five M rings were identified in the case of bismuth (83) and tungsten (74). The N-rings of bismuth were likewise identified. In the case of the heavier elements (barium to molybdenum), the L^{III} level is the most effective in the emission of secondary electrons and L^{I} the least effective, in agreement with deductions from X-ray data. With decreasing strength of binding, the differences between the effects of the different rings become appreciably less pronounced. In the case of strontium, the three L lines are of approximately

equal intensity, whilst with copper L_I is just perceptibly the strongest line. The M and N levels likewise show a similar changing over of high intensity from the "softer" to the "harder" sub-groups. J. S. G. T.

Long-range Particles from Radium-active Deposit. GERHARD KIRSCH and HANS PETTERSSON (*Nature*, 1923, **112**, 687).—A reply to Bates and Rogers (this vol., ii, 720). The difference in brightness between the scintillations from α-particles and those from hydrogen particles, viewed under identical conditions, is so conspicuous that no mistake is possible. A small number of scintillations of the α-type was generally observed in addition to the much fainter hydrogen scintillations, especially at the lowest values of absorption. These particles are for the time being assumed to be identical with those found by Rutherford (A., 1919, ii, 258) to be expelled from oxygen. The former view, that the particles are hydrogen particles expelled by artificial disintegration of the glucinum, magnesium, silicon (and probably also lithium) atoms is upheld. A. A. E.

The Relative Activities of Radioactive Substances in an Unchanged Primary Uranium Mineral. W. P. WIDDOWSON and A. S. RUSSELL (*Phil. Mag.*, 1923, [vi], **46**, 915—929).—The work of Boltwood (A., 1908, ii, 454) on the relative activities of the radioactive constituents of an unchanged primary uranium mineral (pitchblende) has been carefully repeated. The results obtained agree with those previously obtained, indicating the lowness of the relative activity of the mineral to that of its uranium content, but disagree therewith as regards the relative activities of polonium, ionium, radium, and uranium. The values found for these agree closely with those deduced theoretically. The ratio of the activity of the actinium series to that of the radium series is found to be 0·29, in agreement with the result obtained by Hahn and Meitner (A., 1920, ii, 148). J. S. G. T.

The Relative Deposition of Radium and Barium Salts as a Function of Temperature and Acidity. W. B. PIETENPOL (*Physical Rev.*, 1922, **20**, 199).—It is found that the first crystals formed in a radium–barium solution contain a larger percentage of radium than succeeding crystals. The efficiency and rapidity of the separation by fractional crystallisation may be increased by separating the liquor from the crystals at a point above room temperature. With rapid cooling, a smaller percentage of radium is adsorbed than with slow cooling. A. A. E.

Ionisation and Resonance Phenomena. CHARLES B. BAZZONI (*J. Franklin Inst.*, 1923, **196**, 627—651).—Bohr's theory of atomic structure and the mechanism of radiation are briefly reviewed, and experimental determinations of resonance and ionisation potentials, more especially in the cases of helium and mercury, and the excitation of resonance spectra, critically examined in relation to the theory. The author concludes that the impact potentials of helium require further study. J. S. G. T.

The Fundamental Processes concerned in the Thermal Ionisation of Gases. RICHARD BECKER (*Z. Physik*, 1923, **18**, 325—343).—The author discusses the fundamental processes, viz., ionisation due to absorption of radiation, ionisation by electronic collisions, and the disappearance of electrons due to combination either with or without the emission of radiation, concerned in the establishment of equilibrium in a thermally-ionised system, and deduces the equilibrium equation relating to the thermal ionisation of monatomic and univalent gases by the application of statistical mechanics and the quantum theory. J. S. G. T.

New Evidence regarding the Interpretation of Critical Potentials in Hydrogen. P. S. OLMSTEAD (*Physical Rev.*, 1922, **19**, 532—533).—A relatively small amount of atomic hydrogen is produced when a close grid of tungsten wires, introduced close to the gauze in an ionisation tube of the Lenard type, is heated to incandescence. It is shown that the ionising potential of the hydrogen atom is 13·5 volts; the critical potential of ionisation of the molecule, probably without dissociation, is about 11·5 volts, and a weaker effect, ascribed to radiation from the atom, at about 10·2 volts. The strongest effect, dissociation of the molecule and ionisation of one of its parts, is put at 16 volts. A. A. E.

Critical Electron Energies in Hydrogen. FRANK HORTON and ANN CATHERINE DAVIES (*Phil. Mag.*, 1923, [vi], **46**, 872—896). —In continuation of previous work (A., 1920, ii, 215), the authors have made a detailed investigation of the effects of electron collisions with hydrogen, in order to determine more exactly the critical electron energy values, and to ascertain whether the radiation or ionisation occurring at a critical stage is of atomic or molecular origin. The results indicate that critical energy values (expressed in volts) are associated with respective processes as follows: 10·2, $H \longrightarrow H$(excited); 11·9, $H_2 \longrightarrow H_2$ (excited); 12·6, $H_2 \longrightarrow H+H$ (excited); 13·5, $H \longrightarrow H^+ +$ electron; 15·9, $H_2 \longrightarrow H+H^+ +$ electron; 22·8, $H_2 \longrightarrow H_2{}^+ +$ electron; 26·1, $H_2 \longrightarrow H^+ +$ electron$+H$ (excited); 29·4, $H_2 \longrightarrow 2H^+ + 2$ electrons. These deductions are in agreement with the interpretation by Olmstead (this vol., ii, 367) of the critical values observed at 10·2, 12·6, 13·5, and 15·9 volts, but differ in respect of the interpretation of the critical energy stage included between 10·2 and 12·6 volts. The present authors' deduction in this matter is in accord with the value of the resonance potential of normal hydrogen (11·8 volts) deduced by Mohler, Foote, and Kurth (*Physical Rev.*, 1922, **19**, 414) from the consideration of inelastic collision curves. The present experiments establish the existence of a true molecular radiation as distinct from a radiation produced by electronic-molecular encounters at which dissociation and atomic excitation occur. They also support Pauli's suggestion (A., 1922, ii, 703) that the production of positively charged hydrogen molecules requires energy equivalent to about 23 volts. The spectroscopic results obtained are in general agreement with those of Duffendack (this vol., ii, 373), except for the observation of a number of lines of group II of Fulcher's classification,

viz., λλ 5916·8, 5931·6, 5938·9, and 6028·2 Å., which were not observed by Duffendack at 23 volts. Moreover, a visible continuous spectrum of hydrogen can be produced in the absence of the Balmer series lines, and it is suggested that this spectrum originates owing to the formation of molecules (H_2 or possibly H_3) by the combination of neutral atoms. J. S. G. T.

The Lengths of the Free Paths of Slow-moving Electrons in the Rare Gases. H. SPONER (*Z. Physik*, 1923, **18**, 249—257).—Experiments showing that the respective lengths of mean free path of slow-moving electrons in the rare gases, argon, krypton, and xenon increase continuously with decreasing velocity of the electrons until a velocity corresponding with zero accelerating voltage is attained, are described. In the case of krypton at a pressure of 1·2 mm., maximum values of the mean free paths of electrons resulting from inelastic collisions occur when the exciting potential has the value 8·4±0·2 or 9·6±0·2 volts. The corresponding voltages in the case of xenon are 8·0 and 8·8 volts. The ionisation potential of krypton was found to be between 12 and 13 volts; that of xenon was between 11 and 12 volts. J. S. G. T.

The Lengths of the Free Paths of Slow-moving Electrons in the Vapours of Mercury and Cadmium. R. MINKOWSKI (*Z. Physik*, 1923, **18**, 258—262).—The author shows that, as in the case of the rare gases (see preceding abstract and Ramsauer, A., 1921, ii, 324), the respective lengths of mean free path of the slowest-moving electrons in mercury and cadmium vapours depend, although to a considerably less extent, on the velocities of the electrons. In the case of mercury vapour, maximum values of the mean free paths of electrons resulting from inelastic collisions correspond with values of the exciting potential equal to 4·7, 4·9, 9·8, and 11·6 volts. In cadmium vapour, the corresponding values are 3·7, 3·8, 5·4, 7·4, and 7·6 volts. Attention is, in this connexion, directed to the occurrence in the case of cadmium vapour, of the exciting voltage 3·7 volts, correspondng with the series $1S-2p_3$, a result hitherto observed only in the case of mercury vapour. J. S. G. T.

Ionising Potentials of Helium and some Multiatomic Gases. C. A. MACKAY (*Phil. Mag.*, 1923, [vi], **46**, 828—835).—The following values (volts) of the ionising potential have been determined for the respective gases: helium, 24·5; nitrogen, 16·3; hydrogen, 15·8; oxygen, 12·5; hydrogen chloride, 13·8; hydrogen bromide, 13·2; hydrogen iodide, 12·8; ammonia, 11·1; water vapour, 13·2. The value for helium is in agreement with the convergence limit of Lyman's spectroscopic series. The value for oxygen is considerably lower than the value, 15·5 volts, found by Foote and Mohler. J. S. G. T.

The Scattering of Electrons by Aluminium. C. DAVISSON and C. H. KUNSMAN (*Physical Rev.*, 1922, **19**, 534—535; cf. A., 1922, ii, 251).—Analysis of the distribution curves below 200 volts indicates that the *L*-electrons of aluminium are at a distance of about 3×10^{-9} cm. from the atomic nucleus. Above 200 volts the

distribution is complicated by the scattering effect of oxygen atoms on the surface of the target. A. A. E.

Relations between Supplied Energy, Spectral Intensities, and Alterations in Different Media. L. HAMBURGER (*Trans. Amer. Electrochem. Soc.* [advance copy], 1923, 307—318).—From the proportionality between the energy supplied to discharge tubes, the intensities of the spectral lines emitted and the pressure difference due to the transference of ponderable ions in the discharge, the author concludes that atoms both absorb and emit energy in quanta. The part played by partly ionised atoms in the phenomena of electro-luminescence, effects due to collisions of slow-moving electrons with atoms, spectra excited otherwise than electrically, catalytic phenomena, and velocities of reaction are briefly referred to. The dependence of the reduction temperature necessary in the Bucher process for the fixation of nitrogen, on the nature of the carbonate employed is discussed with reference to the ionising and resonance potentials of the alkali and alkaline-earth metals. The unity of optical, chemical, and energy relations contemplated in the quantum theory and the Rutherford-Bohr interpretation of atomic structure indicates that chemical and physical changes do not differ essentially. J. S. G. T.

Problems of Hydrone and Water: the Origin of Electricity in Thunderstorms. G. C. SIMPSON (*Nature*, 1923, **112**, 620; cf. Armstrong, this vol., ii, 772).—It is held to be conclusively proved that if there are ascending currents exceeding eight metres per second in the atmosphere, there must be much breaking of rain drops; that when a water drop breaks there is a separation of electricity; that the broken water drops retain a positive charge; that the air attains a negative charge, and that a considerable excess of positive electricity is brought down by rain. Armstrong's views are considered to be completely untenable. A. A. E.

The Electrical Conductivity of Solid Orthophosphoric Acid. MARK RABINOWITSCH (*Z. anorg. Chem.*, 1923, **129**, 60—66).—The conductivity of orthophosphoric acid, $2H_3PO_4,H_2O$, was studied in the crystalline and supercooled states and found to be of the magnitude of 10^{-4} and 10^{-2}, respectively. The temperature coefficient was positive; a sudden change occurs on solidifying. The decomposition potential is given as 1·70 volts. The ratio of these conductivities is assumed to indicate the degree of loosening of crystal lattices (cf. Hevesy, A., 1922, ii, 623). The conductivity of anhydrous phosphoric acid decreases with the time; this change is associated with some change in the acid. W. T.

The Theory of Electrolytic Ions. XXVIII. The Conductivities of the Arsinic Acids. RICHARD LORENZ and ELISABETH BREHMER (*Z. anorg. Chem.*, 1923, **128**, 76—80).—Continuing previous work (A., 1920, ii, 465; this vol., i, 406), the dissociation or affinity constant has been determined for a number of substituted phenyl-arsinic acids. The constant K is calculated from the formula $\alpha^2/1-\alpha C\,.\,10^{-3}$, and is therefore related to Kohlrausch's constant c,

which is in *C.G.S.* units, thus: $c.10^5=K$. The following values are given for K at the molar concentration 1/256: phenylarsinic, 0·027; *p*-hydroxyphenylarsinic, 0·015; *p*-amino-*o*-tolylarsinic, 0·014; *m*-methoxyacetarsanilic, 0·029; *p*-nitrophenylarsinic, 0·137; *o*-nitrophenylarsinic, 0·037; 2-nitroarsanilic, 0·0086; 3-hydroxyarsanilic acid (at 1/512), 0·0067. In general, the affinity constant of phenylarsinic acid is affected in the same way by substituents as benzoic acid. An exception appears in the cases of *o*-nitrophenylarsinic acid and *o*-nitroarsanilic acid, where the expected augmentation of the affinity constant by the *o*-nitro-group is not realised. On account of the low solubilities of 2-nitroarsanilic and 3-hydroxyarsanilic acids, their conductivities and affinity constants could only be determined at high dilutions and, in the case of the latter, owing to its rapid decomposition at the electrodes, the result is only approximate. E. H. R.

Electrical Resistivity of Commercial Aluminium. LÉON GUILLET (*Compt. rend.*, 1923, **177**, 953—955).—The purest commercial aluminium has a resistivity of 2·8 micro-ohms per sq. cm./cm. Impurities may cause this figure to become even higher than 3·2 (for 89·5% metal). Silicon has a greater effect on the resistivity than iron, whilst mechanical treatment, even cold hammering, only increases the resistivity very slightly, particularly with the purer specimens of aluminium. In tempering, the more rapid the quenching, the higher the resistivity, probably owing to more silicon being retained in solution under these conditions. E. E. T.

Existence of Ions with a Dual Character. OTTO BLÜH (*Z. physikal. Chem.*, 1923, **106**, 341—365).—The dipole theory is briefly discussed, and on the basis of this it is shown that amphoteric electrolytes, so far as they form true ions of dual character, must raise the dielectric constant of the solution containing them. Measurements of the dielectric constant of aqueous solutions of sulphanilic acid, helianthin, *o*-aminobenzoic acid, *p*-aminobenzoic acid, hippuric acid, and benzoic acid show that such dual ions exist in aqueous solutions of amphoteric electrolytes. It is shown that an internal salt and a dual ion are not the same thing. New measurements of the dielectric constant of aqueous solutions of strong electrolytes show that this quantity is lower than that for pure water, a result which accords with the dipole hypothesis, and is opposed to the result of earlier measurements. Water is considered as an amphoteric electrolyte, and the high dielectric constant of this liquid is regarded as a consequence of the presence of dual ions. On the basis of such dual ions, a mechanism of the conduction of an electric current by acids and bases is developed. J. F. S.

Electrical Resistance of Quinoline–Water Systems. MARTIN H. FISCHER (*Kolloid Z.*, 1923, **33**, 208—215).—The electrical resistance of quinoline, solutions of water in quinoline, and of quinoline in water, of all concentrations up to a saturated solution, has been measured at 24°. The effect of the addition of acids, bases, salts, and ethyl alcohol on the electrical resistance has been

measured at 22° and 23°. Pure quinoline has a resistance of 400,000 ohms at 24°, and this value falls regularly with the addition of water to the value 80,000 ohms for the saturated solution. The addition of $N/50$-hydrochloric acid decreases the resistance very much, the amount of decrease being greater the greater the amount of acid added. The addition of $N/50$-potassium hydroxide produces a similar, but smaller, decrease in the resistance. Comparing the effect of various acids on the resistance, it is found that sulphuric acid has the greatest effect, and this is followed in order by hydrochloric, oxalic, acetic, and lactic acids. Of the bases, potassium hydroxide has the greatest effect, and is followed in order by sodium, calcium, and ammonium hydroxides. Salts generally reduce the resistance in a marked degree, as also does ethyl alcohol. These results are practically the same for both the water and the quinoline phases. J. F. S.

Electrometric Measurements with Regard to Ionic Activity. LEONOR MICHAELIS and KOSAKU KAKINUMA (*Biochem. Z.*, 1923, **141**, 394—409).—Electrometric measurements have been made on acid and alkaline, salt and salt-free solutions with the view of determining the relation between ionic concentration and Bjerrum's activity coefficient (A., 1919, ii, 9; 1920, ii, 79) at varying dilutions. Measurements of the potential differences of pure solutions of hydrochloric acid against a standard acetate electrode showed that in concentrations below $M/30$ the activity coefficient of the hydrogen-ions is unity, and the activity is regarded as being equal to the concentration of the acid. The influence of rubidium, potassium, sodium, and lithium chlorides on the activity of the hydrogen-ions in buffered and unbuffered solutions of hydrochloric acid solutions is in the order given, rubidium showing the least and lithium the greatest influence in increasing the activity. Similar determinations of the influence of salts on the activity of hydrogen-ions in alkaline solutions showed the effect to be greater than that observed in acid solutions. For salt-free solutions of sodium hydroxide of concentrations less than $M/30$ the solute is fully dissociated and the activity of the hydroxyl-ions is unity. From the sum of p_H and p_{OH} of solutions of sodium hydroxide ranging in concentration from $M/30$ to $M/3000$ values of the dissociation constant of water were obtained; pk_w^{17} is given as 14·13 and pk_w^{18} as 14·10. It is concluded that on thermodynamical grounds neutral salts are without influence on the dissociation constant of water, but an exact experimental demonstration is not given. J. P.

Amphoteric Elements. J. KASARNOWSKY (*Z. anorg. Chem.*, 1923, **128**, 33—44).—The measurement of the normal potential of the system Te/Te'' presents difficulties which have not yet been surmounted, but by applying Nernst's heat theory to the reaction $H_2Te=H_2+Te+34{,}900$ cal. the value has been calculated to be about $-0·913$ volt. The *E.M.F.* of the system $Te|1$ mol. $Te^{····}|1$ mol. $Te''|Te$ would be 1·48 volts and the ion product $[Te^{····}][Te'']^2$ $0·85 . 10^{-102}$. For the reaction $Te_2'' \rightleftharpoons Te''+Te$, the value of the constant $K=[Te'']/[Te_2'']$ is $0·39 . 10^{-2}$. In a similar

manner, the normal potential of selenium with respect to its bivalent ion, Se/Se'', is calculated to be −0·771 volt. The increasing sensitiveness of sulphides, selenides, and tellurides to oxygen is seen to be in the order of the normal potentials of the three elements, the value for sulphur being −0·55. The value for polonium, extrapolated from that of tellurium, is probably about −1·0 volt. It follows from the extremely small value of the ion products, that a positive ion of an amphoteric element practically cannot exist in presence of negative ions, and *vice versa*. Amphoteric cleavage is a strongly endothermic process. For tellurium, the following values are calculated: $3Te \rightleftharpoons Te^{\cdots\cdot}+2Te''-136{,}000$ cal. and $5Te \rightleftharpoons Te^{\cdots\cdot}+2Te_2''-129{,}000$ cal. The formation of ditelluride can then be expressed by the equation: $Te''+Te=Te_2''+3{,}500$ cal.

E. H. R.

The Potential Surfaces of Ternary Alloys of Cadmium and Mercury with Tin or Lead. ROBERT KREMANN, HERMANN PRAMMER, and LUDWIG HELLY (*Z. anorg. Chem.*, 1923, **127**, 295—315).—The potentials of ternary alloys of cadmium, mercury, and tin and of cadmium, mercury, and lead were measured against a $Hg|N\text{-}CdSO_4$ electrode, and the results obtained are discussed with the aid of diagrams for which the original should be consulted.

H. H.

The Electrochemical Behaviour of Alloys of Iron–Chromium, Iron–Molybdenum, and Iron–Aluminium. G. TAMMANN and E. SOTTER (*Z. anorg. Chem.*, 1923, **127**, 257—272).—The potentials of iron–chromium alloys in $N/10$-sulphuric acid were measured with anodic and cathodic polarisation. Up to 15% of chromium, the potential is negative to chromium in each case, but above that percentage of chromium the alloy is strongly electropositive to chromium with cathodic polarisation, and only slightly so with anodic polarisation. The end potential is not reached immediately, and for anodic polarisation the equation $t=t_0e^{\alpha(\pi-\pi_0)}$ is suggested, where π_0 is the potential at time t_0 and α is a constant. For cathodic polarisation, the case is more complex, there being apparently three distinct periods. Polishing with emery, and heating at 400° decrease the electro-positiveness of the alloys. The presence or absence of air bubbling through the solution affects the potential but little, but the presence of a reducing agent, such as pyrogallol, phosphorus, or quinol, reduces the electropositiveness of cathodically polarised iron–chromium alloys to a remarkable extent. Molybdenum–iron alloys are electronegative to molybdenum up to 65% molybdenum, and then slightly electropositive. For iron–aluminium alloys, the potential slowly falls with time when cathodically polarised, and rises when anodically polarised. It is suggested that passivity depends on the protection of the metal by a layer of oxygen, but that the density of this layer can vary within fairly wide limits.

H. H.

The Galvanic Tensions of Ternary Alloys of Antimony, Zinc, and Bismuth. ROBERT KREMANN, AUGUST LANGSBAUER and HERMANN RAUCH (*Z. anorg. Chem.*, 1923, **127**, 229—238).—The

E.M.F. of some ternary alloys of zinc, antimony, and bismuth were measured against a Zn|*N*-$ZnSO_4$ element. By keeping the ratio bismuth/antimony constant, and varying the proportion of the other component, part of the ternary equilibrium diagram was constructed. Measurements were made with alloys which had been slowly cooled and with the same alloys tempered for twelve hours at 260°. Three cases are distinguished: (*a*) ternary alloys in which the ratio Sb/Zn is less than 40/60 atom.%, which show practically the potential of zinc; (*b*) ternary alloys in which the ratio Sb/Zn lies between 40/60 and 50/50 atom.%, which behave as mixtures of the binary compounds Zn_3Sb_2 and ZnSb with bismuth and show a potential about 50—100 millivolts more positive than zinc, and (*c*) ternary alloys in which the ratio Sb/Zn lies between 50/50 and 100/0 atom.%, which are less noble than zinc. By plotting isopotential lines on the triangular concentration diagram, it is shown that for alloys containing 50/50 atom.% of Zn/Sb, the *E.M.F.* is practically independent of the bismuth content, especially in the case of the tempered alloys. H. H.

The Galvanic Tensions of Ternary Alloys of Bismuth, Cadmium, and Lead. ROBERT KREMANN and AUGUST LANGBAUER (*Z. anorg. Chem.*, 1923, **127**, 239—243; cf. preceding abstract). —The *E.M.F.* of ternary alloys of bismuth, cadmium, and lead were measured against a Cd|*N*-$CdSO_4$ element. Triangular concentration diagrams on which isopotential lines were plotted, were constructed as before, and from the results obtained it is found that the potential of the alloy falls abruptly from that of cadmium to that of lead as soon as the percentage by weight of the former in the alloy falls below 4. Bismuth has very little effect on the *E.M.F.* until the Bi/Pb ratio rises to 98/2, when the *E.M.F.* again falls abruptly to that of bismuth. H. H.

A New Type of Reduction-Oxidation System. I. Cysteine and Glutathione. MALCOLM DIXON and JUDA HIRSCH QUASTEL (T., 1923, **123**, 2943—2953).

Membrane Potentials and Colloidal Behaviour. A. V. HILL (*J. Gen. Physiol.*, 1923, **6**, 91).—A reply to Hitchcock (this vol., ii, 530), in which the author's criticism (this vol., ii, 221) is reiterated. E. S.

Membrane Potentials and Colloidal Behaviour. DAVID I. HITCHCOCK (*J. Gen. Physiol.*, 1923, **6**, 93).—A reply to Hill (cf. preceding abstract). E. S.

Temperature Coefficients of Unsaturated Weston Cells. WARREN C. VOSBURGH and MARION EPPLEY (*J. Amer. Chem. Soc.*, 1923, **45**, 2268—2277).—The *E.M.F.* of unsaturated Weston cells has been investigated. It is shown that the *E.M.F.* increases in an approximately linear manner as the concentration of cadmium sulphate decreases. The *E.M.F.* values are linear functions of the temperature between 15° and 35°, but not between 35° and 45°. The temperature coefficient between 15° and 35° is found to be a

linear function of the *E.M.F.* It decreased from 0·0000028 volt per degree for cells with an *E.M.F.* of 1·01827 volts to −0·000013 volt per degree for cells with an *E.M.F.* of 1·0210 volts. Normal cells with electrodes made by saturating 0·015*M*-sulphuric acid solution with hydrated cadmium sulphate behave in accordance with Wolff's temperature formula. Mercurous sulphate prepared by reduction of mercuric sulphate with formaldehyde at 100° showed no difference in its behaviour in normal cells from the electrolytic salt. The differential heat of solution of hydrated cadmium sulphate in a slightly acid saturated solution has been calculated, and the following values have been obtained for 0·012*M*-sulphuric acid: 15°, −352 cal./mol., 18°, −431 cal./mol, and 25°, −605 cal./mol.

J. F. S.

Action of Light on Electrodes of Metals possessing Low Solution Pressures. RENÉ AUDUBERT (*Compt. rend.*, 1923, **177**, 818—821; cf. Buisson, A., 1900, ii, 519).—Experiments are carried out on the effect of illuminating one of two electrodes formed of the same metal and immersed in the same electrolyte, illumination being effected using an arc lamp (or nitrogen-filled tungsten lamp) with a condenser, and, in some experiments, light filters. Independently of the electrolyte, the illuminated electrode becomes the anode in the case of platinum, copper, and mercury, and the cathode in the case of silver and gold, unless secondary effects (photochemical decomposition of electrolyte, etc.) occur. Thus in presence of ferrous or ferric salts, the illuminated platinum electrode becomes negative or positive, according as oxidation or reduction is dominant, whilst a silver electrode, in hydrochloric acid solution, is covered with silver chloride when illuminated.

Blue rays are much more active than red ones. The sensitivity of metals varies inversely with their solution pressures, and for each metal there appears to be a threshold of excitation which, as metals more and more electropositive are considered, is displaced towards higher frequencies.

The effects produced are independent of the anion, and appear to depend on the layer of kations adsorbed on the electrode, and on the solution-pressure of the kation. E. E. T.

Intermittent Current Electrolysis. II. Overvoltage Study of the Lead Electrode. SAMUEL GLASSTONE (T., 1923, **123**, 2926—2934).

Note on Glasstone's Discussion of Over-voltage Measurement. HERBERT HAWLEY and HENRY JULIUS SALOMON SAND (T., 1923, **123**, 2891—2901).

Ions and Ionic Activity. P. DEBYE (*Chem. Weekblad*, 1923, **20**, 562—568).—A repetition of the criticisms already advanced against the theory of Ghosh by Prins (this vol., ii, 369) and the author (this vol., ii, 724). The conception of an "electrical atmosphere" round the ion is developed from considerations of energy and potential; the formulæ obtained give values different from, but of the same order of magnitude as those deduced by Ghosh. Mathe-

matical treatment indicates that for a completely dissociated solution the osmotic pressure is determined not only by the concentrations, but also by the valencies of the ions. The addition of a second salt, B, to a system consisting of a saturated solution of one salt, A, with excess of undissolved A, is considered from the energy point of view, and equations are deduced. S. I. L.

Moving Boundary Method for Determining Transport Numbers. DUNCAN A. MACINNES and EDGAR REYNOLDS SMITH (*J. Amer. Chem. Soc.*, 1923, **45**, 2246—2255).—The Denison and Steele method of determining transport numbers (A., 1903, ii, 709; 1906, ii, 68, 329) has been investigated, and a modification developed which involves only a single moving boundary. It is shown that the boundaries move with the theoretical velocities only when the two solutions in contact at a boundary are adjusted to within about 5%, to the relation $C/T=C'/T'$, in which C and C' are the concentrations and T and T' are the transport numbers. The correct value of the transport number can therefore be obtained by a series of experiments approaching more and more closely to this relation. Unless the adjustment is obtained, the results are not independent of the composition of the indicator solution, or of the current passing through the apparatus, and may vary widely and erratically from the true values. The transport numbers at 25° have been determined for $0{\cdot}1N$-solutions of potassium chloride and potassium bromide, using lithium bromide as indicator solution. The transport number of potassium in potassium chloride is found to be $0{\cdot}492\pm0{\cdot}001$ at 25° and in potassium bromide 0·485. These values are compared with the values of Denison and Steele and others. It is shown that the conductivity of the potassium-ion is the same in these two solutions if the correction for viscosity is made. J. F. S.

The Position of Tellurium in the Voltaic Series. J. KASARNOWSKY (*Z. anorg. Chem.*, 1923, **128**, 17—32).—When tellurium is used as cathode in the electrolysis of potassium hydroxide it dissolves as a univalent element, forming potassium ditelluride, K_2Te_2. On the other hand, used as anode in the electrolysis of hydrochloric acid, tellurium passes into solution as a quadrivalent metal, forming $TiCl_4$. The author has measured the normal potential of tellurium corresponding with the two ions Te_2'' and $Te^{····}$. The potential of the system Te/Te_2'', determined in potassium hydroxide solution, varies with the concentration according to Nernst's equation; the normal potential is $-0{\cdot}818$ volt. The normal potential of the system $Te/Te^{····}$ is $+0{\cdot}549\pm0{\cdot}001$ volt. This is the first example of the determination of the normal potentials of an amphoteric element with respect to its positive and negative ions. As a metal, tellurium comes between copper (0·34) and silver (0·80), whilst it is the "noblest" of the metalloids, so far as they have yet been measured. The hypothetical system $Te|N\text{-}Te^{····}/N\text{-}Te_2''|Te$ should have an $E.M.F.$ of 1·37 volts, and the ion product, calculated from van't Hoff's equation, is $[Te^{····}][Te_2'']^2=10^{-95}$.

This gives a measure of the amount of dissociation of tellurium into positive and negative ions. E. H. R.

Electrolytic Separation [Deposition] of Alloys. A. H. W. ATEN (*Rec. trav. chim.*, 1923, **42**, 931—938).—A theoretical discussion of the possibility of depositing an alloy by electrolysis. The problem resolves itself into one of discovering a solution of such a composition that the anode will dissolve in the same proportions as the metals are deposited on the cathode. It is not necessary that the anode shall have this composition. The author concludes that the problem, although difficult, may be capable of solution. H. H.

Chemical Effects Produced by Passing Electric Currents through Thin Artificial Membranes of High Resistance. R. S. LILLIE and S. E. POND (*Proc. Amer. Physiol. Soc., Amer. J. Physiol.*, 1923, **63**, 415—416).—An electric current corresponding with a potential of 10 volts flowing across a caoutchouc membrane of thickness 40 μ interposed between two electrolyte solutions, one of which is a mixture of ferrous chloride and potassium thiocyanate, causes oxidation of ferrous to ferric iron at the surface of the membrane facing the cathode. CHEMICAL ABSTRACTS.

Anomalies of Chromium and its Behaviour during Electrolysis by Alternating Current. N. ISGARISCHEV and A. OBRUTSCHEVA (*Z. Elektrochem.*, 1923, **29**, 428—434).—The solubility of chromium electrodes in acid, alkaline, and neutral solutions, using direct and alternating current and both types of current simultaneously, has been investigated. The solubility of chromium in sulphuric acid at various temperatures and in the presence of various anions has also been investigated. It is shown that there is no definite transition point at which passive chromium passes into the active condition, as is the case in allotropic changes. The metal can become active at any temperature, the activation depending on the properties of the medium. Chromium is rendered passive by exposure to air, by the action of oxidising agents such as chromic acid, hydrogen peroxide, and potassium permanganate, and by the action of electrolytic oxygen; it is rendered active by electrolytic reduction and by mechanical purification of the surface. Consequently, the passivity of chromium is connected with the formation of a protecting oxide film on the surface. The protecting film is a transparent, colloidal substance, the density and permanence, and consequently the passivating action, of which depend on the nature of the medium, particularly on the presence of those ions, such as chloride- and bromide-ions, which bring about colloidal transitions. Chloride-ions have the greatest disturbing effect on the film and make it permeable to most reagents. Particles of passive chromium become active when brought into contact with active chromium, zinc, or magnesium. Since these metals are all more electronegative than passive chromium, this action is due to the formation of a galvanic element which liberates hydrogen and consequently reduces the oxide film. The oxide film is also the cause of the

anomalies of chromium. Chromium dissolves as anode to give bi-, ter-, and sexa-valent ions, the amounts of the various types of ion depending on the conditions. J. F. S.

The Electrochemistry of the High Intensity Arc. PRESTON R. BASSETT (*Trans. Amer. Electrochem. Soc.* [advance copy], 1923, 319—338).—The phenomena exhibited by various types of electric arcs operated with currents ranging from 20 to 300 amperes are briefly described. The tendency to produce two arc flames, a positive and a negative, is present in practically all arcs, and in the high-intensity arc this tendency is enhanced, so that the two flames are separate and distinct, and each flame performs a separate function, the positive flame operating as light producer, and the negative as arc maintainer. The positive electrode consists of a core of cerium fluoride and carbon surrounded by a shell of non-graphitisable pure carbon. The negative carbon electrode contains a core of soft carbon. The arc is customarily operated with a current of 150 amperes. The intrinsic brilliance of the arc is from 500 to 1,000 candles per sq. mm., and its temperature about 4,700°. It is suggested that the high intrinsic brilliance of the arc is attributable to the formation of cerium carbide in the arc. J. S. G. T.

Thermal Conductivities of some Metals in the Solid and Liquid States. W. BYRON BROWN (*Physical Rev.*, 1923, 22, 171—179).—In the guard ring method of measurement employed, a cylinder of the metal, electrically heated at one end, was surrounded by a slate tube and a hollow brass cylinder, also heated electrically at one end. The other ends were cooled with running water, and the conductivity calculated from the energy applied to the rod and the temperature gradient. Tables and curves are given for the conductivity of tin, cadmium, thallium, and tin-zinc, tin-lead, lead-antimony, and lead-bismuth alloys. For the pure metals, the following values are abstracted. Tin: 50°, 0·1428; 102°, 0·1404; 209°, 0·1297. Cadmium: 45°, 0·200; 99°, 0·209; 240°, 0·239. Thallium: 45°, 0·0934; 90°, 0·0958; 113°, 0·0976; 125°, 0·0919; 149°, 0·0927. A polymorphic change in thallium at 120° is thus indicated. A. A. E.

Entropy of Diatomic Gases and Rotational Specific Heat. RICHARD C. TOLMAN and RICHARD M. BADGER (*J. Amer. Chem. Soc.*, 1923, 45, 2277—2285).—A direct mathematical method has been developed for determining the theoretical values of the constants S_2 and $C_{298\cdot 1}$ in the equations for the entropy of diatomic gases, $S=7/2R\log_e T+3/2\log_e M-R\log_e p+R\log_e J+S_2$; $S_{(298\cdot 1, 1\text{ atm})}=3/2R\log_e M+R\log_e JC_{298\cdot 1}$. Six different hypotheses which have been proposed for rotational specific heat all based on the first form of quantum theory, but based on different hypotheses as to a priori probabilities and as to the lowest possible azimuthal quantum number, have been used to determine the theoretical values of S_2 and $C_{298\cdot 1}$, and the results compared with the experimental values. In the absence of further evidence, the best values for S_2 and $C_{298\cdot 1}$ are 64·92 and 104·57, respectively, the

units being, entropy in calories, temperature in degrees centigrade absolute, pressure in atmospheres, molecular weight in g./mol., moment of inertia in g.cm.^{2}/mol. J. F. S.

The Form of the Melting-point Curves of Series of Binary Mixed Crystals, and the Lattice Parameters of their Components. EUSTACE J. CUY (*Z. anorg. Chem.*, 1923, **128**, 241—244).—The maximum departure from the straight line joining the melting points of the components of the curve of the beginning of crystallisation, a temperature range ΔTm, has been plotted against the relative difference of the two lattice parameters, Δd, given by the expression $\Delta d=(d_A-d_B)/(d_A/2+d_B/2)$, where d_A and d_B are the parameters of the two components, A and B, for a series of pairs of halides of the alkali metals, and some alloys. The points found lie on a straight line, which for the value $\Delta Tm=0$ (*i.e.*, when the temperature of beginning of crystallisation lies on the line joining the melting points of the two components) cuts the Δd axis at the value 0·04. S. I. L.

Cryoscopy in $Na_2SO_4,10H_2O$. Molecular Magnitudes of Malates, Molybdates, and Molybdomalates. E. DARMOIS and J. PÉRIN (*Compt rend.*, 1923, **177**, 762—765; cf. A., 1922, i, 220, 522; Löwenherz, A., 1896, ii, 149, and Boutaric and Leenhardt, A., 1912, ii, 1136).—Sodium sulphate decahydrate is used as a cryoscopic solvent, k being calculated from a study of the $\Delta t/c$-Δt curves for carbamide, sodium chloride, and sodium nitrate. The value of k so found, namely, 32, is then made use of in determining the molecular complexity of various sodium salts, the results being as follows: Sodium malate, $C_4H_5O_5Na$, sodium molybdate, Na_2MoO_4, sodium "acid" molybdate, $Na_6Mo_7O_{24}$; sodium dimolybdomalate (hexahydrate) (M found, 1010) is derived from a tetramolybdic acid whilst sodium molybdodimalate (M found, 427) is derived from 2 mols. of malic acid (cf. Klason, A., 1901, ii, 162). Whereas the sodium salts give true molecular weights in sodium sulphate solution, the corresponding ammonium salts are completely dissociated as in aqueous solution. E. E. T.

The Accurate Determination of Elevation of Boiling Point. KAZIMIERZ JABŁCZYŃSKI and STANISŁAW KON (T., 1923, **123**, 2953—2963).

Vapour Pressure of Monatomic Elements. RUSSELL W. MILLAR (*J. Amer. Chem. Soc.*, 1923, **45**, 2323—2329).—A theoretical paper in which a formula has been derived by means of which the pressure of a monatomic gas in equilibrium with the liquid or solid element can be calculated from specific heat data and one vapour pressure measurement, the latter being required to evaluate the integration constant Z. The equation in its general form is $\log p(\text{atm.}) = (2{\cdot}5-[a-\beta]/R)\log T - 2{\cdot}303\beta/2R \, . \log T^2 + Z/T + 1/R[1{\cdot}5R\log w + \alpha\log T_0 + 2{\cdot}303\beta/2\,(\log T_0)^2 - (2{\cdot}63 + S_0 - (\alpha-\beta) + 2{\cdot}5R)/2{\cdot}303]$. This formula has been evaluated for mercury, zinc, sodium, and hydrogen. In the case of mercury, it takes the form $\log p(\text{mm.}) = -0{\cdot}8443\log T - 3319{\cdot}6/T + 10{\cdot}5134$, and reproduces the

observed values with fair accuracy. For sodium, the equation is $\log p(\text{mm.}) = -1{\cdot}20 \log T - 5135/T + 11{\cdot}071$, and in this case the agreement of the calculated value with the experimental value is very much better at low temperatures than at higher temperatures. In the case of zinc, the equation is $\log p(\text{mm.}) = 4{\cdot}0583 \log T - 0{\cdot}7845 (\log T)^2 - 6823{\cdot}1/T + 3{\cdot}7555$, which reproduces the experimental values with fair accuracy up to 363°. Hydrogen, below 60° Å., has the heat capacity of a monatomic gas. The formula in this case is $\log p(\text{mm.}) = 7{\cdot}3725 \log T - 2{\cdot}0572 (\log T)^2 - 26{\cdot}8679/T - 1{\cdot}9280$, which gives fair agreement. J. F. S.

Free Energy of the Thiosulphate-ion. F. Russell Bichowsky (*J. Amer. Chem. Soc.*, 1923, **45**, 2225—2235).—A complete thermodynamic investigation of the reaction $S + CaSO_3,2H_2O = CaS_2O_3$ aq $+ 2H_2O$ has been carried out. The reaction is shown to be reversible, and the equilibrium constant has been determined at 141°, 122°, 110°, 100° and 79·8°. Calcium thiosulphate, $CaS_2O_3,6H_2O$ dissolves in water at 25° to the extent of 2·28 g. of the crystallised salt per 1,000 g. of solution. The heat of the reaction has been determined experimentally as well as the specific heat, freezing point, and heat of dilution of solutions of calcium thiosulphate. The solubility of the dihydrate of calcium sulphite has been determined at 25°, and the mean value 0·000037 g. mols. per litre obtained. Using the data obtained in the present investigation and other data, the free energy of formation, ΔF_{298}, of the thiosulphate-ion is calculated to be −125,110 cal. J. F. S.

The Heats of Combustion of Benzoic Acid, Naphthalene, and Sucrose. P. Schläpfer and W. Fioroni (*Helv. Chim. Acta*, 1923, **6**, 713—729).—The ratios between the heats of combustion of benzoic acid, naphthalene, and sucrose were determined with great exactitude for the purpose of using these substances as calorimeter standards. The heat of combustion of benzoic acid was taken as 6324 cal. per gram weighed in air, and this value was used for determining the water equivalent of the calorimeter. The value so obtained was used in determining the heats of combustion of naphthalene and sucrose both by the ordinary method and the adiabatic method. The most probable values are: naphthalene 9613·7, and sucrose 3945·7 cal. per gram. E. H. R.

The Adiabatic Cooling of Water and the Temperature of its Maximum Density as a Function of Pressure. Nicolai Antonovitch Pushin and Elijah Vasiljevich Grebenshchikov (T., 1923, **123**, 2717—2725).

Some Thermal Properties of Gases. I. Density of the Coexistent Phases of Dimethyl Ether. Ettore Cardoso and Augusto Acquaviva Coppola (*J. Chim. Phys.*, 1923, **20**, 337—346).—The density of the liquid and gaseous phases of dimethyl ether have been experimentally determined from 0·20° to 126·50°. Extrapolation of the value for 126·90°, that is, for the critical temperature, leads to the value 0·2714±0·0003 for the critical density. J. F. S.

Some Thermal Properties of Gases. II. Critical Constants and the Vapour Pressure of Dimethyl Ether. ETTORE CARDOSO and ALFREDO BRUNO (*J. Chim. Phys.*, 1923, **20**, 347—351; cf. preceding abstract).—The critical pressure and temperature and the vapour pressure of dimethyl ether have been determined at temperatures 126·9° to 0·0°. The following experimentally determined data are recorded: $t_c=126·90°\pm0·05°$, $p_c=52·00\pm0·05$ atm., vapour pressure at 122·20°, 47·67 atm.; 117·80°, 44·06; 116·82°, 43·41; 113·75°, 41·24; 110·57°, 38·82; 99·90°, 32·14; 90·25°, 26·80; 80·10°, 22·14; 64·68°, 15·95; 56·02°, 13·11; 49·75°, 11·22; 46·13°, 10·31; 33·55°, 7·49; 25·40°, 6·05; 16·80°, 4·58; 9·25°, 3·58; 0·00°, 2·52. The vapour pressure is expressed by the equation $\log p=0·40654+0·016082t-0·000069963t^2+0·00000019343t^3$. The differential coefficient is given by $dp/dt=p(0·037031-0·00032220t+0·0000013362t^2)$. J. F. S.

Wetting of Glasses by Mercury. EARLE E. SCHUMACHER (*J. Amer. Chem. Soc.*, 1923, **45**, 2255—2261).—An attempt has been made to cause mercury to wet glass and quartz after their surfaces have been freed from gas by heating at 550° in a vacuum. Fairly good wetting can generally be obtained on quartz after this treatment, but it can only be obtained occasionally on Pyrex glass and on lime soda glass. The difficulty in causing mercury to wet glass appears to become greater as the alkali-content of the glass becomes greater. The term "wetting" is used in the sense that wetting is complete when the angle of contact between liquid and solid is zero and the meniscus is concave, and that the liquid does not wet the glass in cases where the angle of contact is zero and the meniscus is convex. In the present work, wetting was considered to have taken place when the meniscus of the mercury was less convex at the conclusion of the experiment than it was at the start. J. F. S.

The Nature of Charcoal "Sorption." H. HORTON SHELDON (*Physical Rev.*, 1922, **19**, 253).—The dual nature of sorption (McBain, A., 1919, ii, 449) by charcoal is demonstrated by the fact that when the pressure–time curve for gases, or the concentration–time curve for solutions, is plotted, there are evidently two distinct parts separated by a bend. The second action, however, begins only after the first is nearly complete. Since solution should begin as soon as adsorption, it is suggested that the second part is due to diffusion into the more inaccessible channels; this cannot be expected to take place to any extent until the easily accessible or directly exposed portions are saturated. A. A. E.

Adsorption of Uranium-X_1 and Thorium by Charcoal. H. FREUNDLICH and MARIE WRESCHNER (*Z. physikal. Chem.*, 1923, **106**, 366—377).—Uranium-X_1 is completely adsorbed by charcoal from a solution of a uranium salt, but if a small quantity of a thorium salt is added the uranium-X_1 is not adsorbed at all. It was shown previously that if the thorium nitrate used in the above experiment is previously shaken with charcoal, it loses, to a great extent, its power of displacing the adsorption of uranium-X_1 (A.,

1916, ii, 70). This result is confirmed in the present paper; it is also shown that a solution of thorium nitrate which has been shaken with charcoal behaves like a solution of thorium nitrate which has passed through a dialysis membrane or one from which the colloidal particles has been removed by cataphoresis. This leads to the view that the colloidal particles in thorium nitrate are responsible to a large extent for the displacement of the adsorption of uranium-X_1 by charcoal, and that when these particles are removed by adsorption, dialysis, or cataphoresis the displacing action of thorium nitrate ceases. This explanation is in keeping with the fact that when an acid, colloid-free solution of thorium nitrate after treatment with charcoal is evaporated to dryness and redissolved, it has the same displacing effect as an untreated solution of thorium nitrate. The explanation is that the colloid particles are not removed from acid solutions by charcoal, and on solution after evaporation these are again peptised. Uranium-X_1 is also partly adsorbed as colloidal particles, and this would explain the very long time required for setting up the adsorption equilibrium and the reversible nature of the displacement by thorium, whilst other adsorptives such as benzoic acid and strychnine nitrate are not reversibly displaced. J. F. S.

Adsorption. III. Peptisation and the Reversal of the Charge on some Hydroxides. K. C. SEN and N. R. DHAR (*Kolloid Z.*, 1923, **33**, 193—202; cf. A., 1922, ii, 205).—The peptisation of the hydroxides of iron, mercury, cobalt, copper, nickel, manganese, cadmium, thorium, and cerium by means of solutions of non-electrolytes such as sucrose, dextrose, lævulose, galactose, lactose, mannose, dextrin, starch, and glycerol, has been investigated, in most cases quantitatively. It is found that peptisation only takes place when the alkali hydroxide is added to a mixture of a salt of the metal and the peptising agent. In some cases, it is found that a slight excess of alkali over that required for the formation of the hydroxide assists the peptisation. An increase in the concentration of the salt requires a proportional increase in the peptising agent for complete peptisation. In all cases, the peptisation is chiefly specific, although there is a similarity in the action of the various peptising agents. It is found generally that the hydroxide prepared from sulphates, that is, in the presence of sulphat-ions, is less easily peptised than the same hydroxide in the presence of chloride- or nitrate-ions. Freshly precipitated ferric hydroxide passes into a negatively charged colloid in the presence of arsenious acid. In the presence of an excess of alkali and either glycerol or sucrose, the charge of the colloid is negative, but on adding the alkali slowly to a mixture of ferric chloride and sucrose or glycerol the colloid passes through three definite stages. At first it is positively charged, then it coagulates, and finally it passes into a negative colloid. J. F. S.

The Dissociation Constant of Lithium Hydroxide and the Second Dissociation Constant of Salicylic Acid. I. M. KOLTHOFF (*Rec. trav. chim.*, 1923, **42**, 969—972).—The "dis-

sociation constant" of lithium hydroxide was found to be approximately 0·5. Sodium salicylate may be supposed to ionise in two stages: $OH\cdot C_6H_4\cdot CO\cdot OH \rightleftharpoons Na^{\cdot} + OH\cdot C_6H_4\cdot CO\cdot O'$ and $OH\cdot C_6H_4\cdot CO\cdot O' \rightleftharpoons O'\cdot C_6H_4\cdot CO\cdot O' + H^{\cdot}$. For the second of these equilibria, the dissociation constant is $3{\cdot}6 \times 10^{-14}$. H. H.

The [Second] Dissociation Constant of the Hydroxides of the Alkaline Earth Metals. I. M. KOLTHOFF (*Rec. trav. chim.*, 1923, **42**, 973—979).—The second dissociation constant, that for the equilibrium $MOH^{\cdot} \rightleftharpoons M^{\cdot\cdot} + OH'$, was measured for the hydroxides of barium, strontium, calcium, and magnesium. The values found were: $Ba(OH)_2$, $0{\cdot}19 \pm 0{\cdot}02$; $Sr(OH)_2$, $0{\cdot}15 \pm 0{\cdot}01$; $Ca(OH)_2$, $0{\cdot}086 \pm 0{\cdot}005$; $Mg(OH)_2$, $0{\cdot}004 \pm 0{\cdot}001$. H. H.

Nature of Non-dissociated Acids. H. VON HALBAN (*Z. Elektrochem.*, 1923, **29**, 434—444).—A theoretical paper in which the author discusses and criticises Hantzsch's theory of ionisation (this vol., ii, 475). It is shown that Hantzsch's conception of the pseudo-acid may not be extended to acids generally, nor may it be applied to electrolytes as a whole. J. F. S.

Kinetic Theory of Osmotic Pressure. GÉZA SCHAY (*Z. physikal. Chem.*, 1923, **106**, 378—385).—A theoretical paper in which, on the basis of van der Waals's views, a kinetic hypothesis of solutions of non-electrolytes is developed, and in this connexion it is shown that cause of the osmotic phenomena is not to be sought in a pressure exerted by the dissolved molecules, but rather in a pressure difference of the solvent. The osmotic pressure formula put forward by Sackur has been developed theoretically, and two other possible formulæ have been derived. J. F. S.

Concentrated Salt Solutions. R. O. HERZOG and W. BERGENTHUN (*Annalen*, 1923, **433**, 117—121).—The addition of a small quantity of sucrose to a solution of calcium chloride of about $7N$-concentration causes an increase in the boiling point which is less than that calculated by Raoult's equation. The boiling point of a more concentrated solution is, however, decreased, whilst for certain concentrations there is no effect. A depression of the boiling point is observed when lactose or mannitol is added to $8{\cdot}09N$-calcium chloride, or when dextrose is added to a $8{\cdot}09N$-solution; also by the addition of sucrose to solutions of lithium chloride or calcium thiocyanate. Very little departure from the calculated increase in boiling point is observed when sugar is added to $5{\cdot}3N$-sodium chloride solution. A series of figures is quoted for calcium chloride solutions. Since the work of dilution and the heat of dilution are practically equal, conclusions respecting the nature of the complexes formed cannot be drawn without the aid of further assumptions.

The distribution of cellobiose octa-acetate between chloroform and calcium thiocyanate of the normalities, 90·8, 8·68, and 7·90, has been measured. For a given concentration of salt solution the partition coefficient remains constant; the relative solubility in the aqueous solution decreases rapidly with the concentration of the salt. W. S. N.

X-Rays and Crystal Structure. SIR W. H. BRAGG (*Nature*, 1923, **112**, 618).—A brief discussion of the facts revealed by the X-ray method of crystal analysis, and the limitations of the method. The significance of the term "molecule" is considered in relation to crystal structure. A. A. E.

[X-Ray Analysis of Crystals.] SIR W. H. BRAGG (*J. Franklin Inst.*, 1923, **196**, 675—677).—In reply to adverse criticism by Wyckoff (this vol., ii, 300) of the results obtained by the method of X-ray analysis of crystals, on the ground that this method pays insufficient attention to the theory of space groups, the author points out that whereas the older methods, depending on observations of form, enable the class of a crystal nearly always to be determined, but not its space-group, the method of X-ray analysis likewise enables the crystal class to be determined, and in addition permits, in a large number of cases, data referring to the appropriate space group being ascertained. The conclusions of mathematical crystallography can only prove the possibility of what X-rays actually find, and the author contends that it is unreasonable to reject results because they have been obtained without the use of the terms of the theory of space-groups, since the terms naturally used in X-ray analysis are equally effective in expressing the laws of symmetry. The argument is supported by reference to resorcinol, assigned on the basis of its asymmetric molecular structure, ascertained by X-ray analysis to the space-group C_{2v}^{10}. In the absence of knowledge of the asymmetric character of the molecule, the crystal might equally well be assigned to the space group Q_h^{12}. J. S. G. T.

Stability, in Presence of Water, of a certain Number of Binary Mixtures. N. PERRAKIS (*Compt. rend.*, 1923, **177**, 879—882).—A determination of the quantity of water, which, added to a definite weight of a binary mixture, at constant temperature, causes the appearance of a second layer. The mixtures chosen were: (*a*) ethyl alcohol with one of the following: diphenyl ether, benzene, *o*-cresol, or phenol, (*b*) benzene with one of the following: methyl, ethyl, *iso*propyl, or *n*-butyl alcohols. The results are discussed in terms of miscibility and solubility relationships. E. E. T.

Liesegang Rings. III. Effect of Light and Hydrogen-ion Concentration on the Formation of Colloidal Gold in Silicic Acid Gel. Rhythmic Bands of Purple of Cassius. EARL C. H. DAVIES (*J. Amer. Chem. Soc.*, 1923, **45**, 2261—2268; cf. A., 1922, ii, 140).—A number of experiments are described which show that gels made with silicic acid and gold chloride and a reducing agent are remarkably affected by light, the effect being the production of a banded structure. The light of small wave-length is the active portion of the light in producing these effects. The results obtained in the present work remove Bancroft's objection ("App. Colloid Chemistry," p. 259), to Holmes's diffusion hypothesis of Liesegang ring formation (A., 1918, ii, 392). A further series of experiments shows that there is a distinct relationship between the hydrogen-ion concentration and the size of the "pockets"

in which the gold is formed. The effect of light on the reduction of gold is well shown by the following experiment. To 25 c.c. of $3N$-hydrochloric acid, 2 c.c. of 1% solution of gold chloride are added, and then slowly and with shaking 25 c.c. of water glass (d 1·16). The liquid is filtered into test-tubes and allowed to set for three days. It is then covered with black paper and 5 c.c. of saturated oxalic acid solution are added to each tube, and placed in a dark room for three weeks for diffusion to take place. When a tube is brought into bright sunlight, when first opened there will be only a few crystals of gold, but after fifty seconds' exposure to light there will be a flash of colour in the tube. Narrow but rhythmic bands of purple of Cassius may be obtained as follows. To one of the tubes of gel described above add 3 c.c. of a mixture of 10 g. of anhydrous stannous chloride and 0·1 g. of stannic chloride in 90 c.c. of water, and allow to diffuse, when bands will be produced.

J. F. S.

High-speed Stirring as an Aid to Chemical Action. C. H. Milligan and E. Emmet Reed (*Ind. Eng. Chem.*, 1923, **15**, 1048—1049).—The speed of many chemical reactions depends on (1) the speed of mutual solution of the reagents, (2) the reaction velocity. If the former is greater than the latter, as in the action of sulphur dioxide on benzene in presence of aluminium chloride, then the progress of the reaction is unaffected by stirring. An investigation of the reverse case as exemplified by the absorption of ethylene in benzene in presence of aluminium chloride and the absorption of hydrogen in cotton-seed oil in presence of nickel gave results showing great acceleration; this is expressed by the equation $v = a + br$, in which v is the rate of gas absorption and r the rate of stirring. In these experiments, the speed of the stirrer head, which was a perforated disk with bell-shaped projection underneath, into which the gas was delivered, was varied between 0 and 14,000 r.p.m.

C. I.

The Radiation Hypothesis of the Velocity of Chemical Reaction. A. Kiss (*Chem. Weekblad*, 1923, **20**, 585—589).—By applying to the recent results deduced from the quantum theory by Perrin and others the formula of Arrhenius for the dependence of reaction velocity on temperature, namely $k = se^{-a/T}$, where s and a are constants, the equation $Q/RT^2 = \rho/T^2(\nu_2 - \nu_1)$, where ν_2 and ν_1 are the frequencies of the radiations bringing about the forward and backward changes in a reversible monomolecular reaction, ρ is Planck's constant $0{\cdot}5 \times 10^{-10}$ (*C.G.S.*), and T the absolute temperature, is deduced. This equation for a reversible unimolecular change is independent of the nature or number of molecular collisions, but in applying the same reasoning to reactions of a higher order, the latter factors must be taken into account. From the kinetic theory, regarding molecules in collision as new molecules, equations can be deduced in the same way for these reactions also.

The frequencies of the activating radiations may thus be deduced from the heats of reaction, and checked by the absorption spectra.

The theory indicates that an exothermic reaction is much more sensitive to temperature change than an endothermic reaction.

S. I. L.

A Homogeneous Gas Reaction. The Thermal Decomposition of Chlorine Monoxide. I. CYRIL NORMAN HINSHELWOOD and CHARLES ROSS PRICHARD (T., 1923, **123**, 2730—2738).

Two Heterogeneous Gas Reactions. CYRIL NORMAN HINSHELWOOD and CHARLES ROSS PRICHARD (T., 1923, **123**, 2725—2729).

The Velocity of the Action of Oxygen, Nitric Oxide, and Nitrous Oxide on Metals. E. SCHRÖDER and G. TAMMANN (*Z. anorg. Chem.*, 1923, **128**, 179—206).—The rate of oxidation of iron and nickel, as measured by the formation of films at high temperatures on thin plates (this vol., ii, 831), in an atmosphere of oxygen, is independent of the pressure, except at very low pressures; the initial velocity at the same temperature, plotted against the pressure of the gas, gives a curve very similar to the adsorption isotherm of gases by charcoal, indicating that the oxygen is adsorbed by the surface film of oxide. With copper, on the other hand, oxidation is more rapid at low pressures than at high pressures; whilst at the beginning the rate of formation of the oxide skin is lower at low pressures, this skin is permeable to the gas at low pressures, but becomes impermeable at high pressures, so that the velocity of oxidation rapidly falls off as the pressure rises.

At normal pressure, the rate of oxidation of iron in air, oxygen, or nitric oxide is the same at equal temperatures; in nitrous oxide, the rate is lower. The action of both nitric and nitrous oxides on nickel gives rise at first to a slightly permeable skin, which becomes permeable at a definite thickness, 280 $\mu\mu$ measured as air (to obtain absolute thickness, d vide by the coefficient of refraction of the oxide film), after which the course of the action becomes similar to that in a mixture of oxygen and nitric oxide in which the partial pressure of the oxygen is greater than 150 mm. S. I. L.

The Discontinuity of the Hydration Process. WILLIAM A. DAVIS and J. VARGAS EYRE (*Proc. Roy. Soc.*, 1923, [*A*], **104**, 512—537).—The authors have determined the rates of hydration of very different substances, including salts, *e.g.*, calcium sulphate, copper sulphate, and gelatin and fibrous forms of cellulose. The results indicate that under the same conditions of relative humidity the hydration curves for different substances differ very considerably in character. Thus in the case of copper sulphate, the curve showing the percentage of moisture absorbed at short intervals is characterised by long linear portions and short parabolic arcs. The curve for calcium sulphate shows a preponderance of parabolic portions, whilst cellulosic materials are characterised by the almost complete absence of linear portions of the hydration curve. Substances exposed in an atmosphere saturated with water vapour give entirely different hydration curves from those obtained when the same substances are exposed in a drier atmosphere, *e.g.*, 88% humidity.

In some cases, hydration may proceed at a slower rate, over a long period of time, in the atmosphere of greater humidity. Notwithstanding the tendency of a powdery anhydrous salt to "set" to a hard cake as hydration proceeds, the rate of hydration is not affected. The "set" mass continues to absorb water, as though it existed in the form of an open-mesh structure freely permeable to water vapour. Empirical equations for successive parabolic portions of the hydration curves are deduced by simple graphical methods. J. S. G. T.

Chemical Dynamics of Autocatalytic Processes. Dynamics of the Oxidation of Arsenious Acid by Bromic Acid. JERZY STANISLAW CHODKOWSKI (*Roczniki Chemji*, 1923, **2**, 183—270).—It has been suggested by Schilov (A., 1903, ii, 276) that the oxidation of arsenious acid by bromic acid is too slow to be measurable except in the presence of sulphurous acid, although in the presence of excess of hydrogen-ions the reaction begins after a long period of induction. It is now shown that at 40°, in the presence of an excess of hydrogen-ions, the reaction proceeds spontaneously and at a measurable rate; the reaction is an autocatalytic one of the second order, according to the equation $dx^1/dt=kax^1\ (1-x^1)$; the velocity constant is equal to 9·7 at 30·7° and in presence of 1/10 mol. of sulphuric acid. The arsenious acid does not appear to exert any influence on the reaction and merely acts as an indicator of the reaction between bromic and hydrobromic acid; the products of this reaction, bromous and hypobromous acid, then oxidise the arsenious acid present. The initial production of hydrobromic acid must, however, be due to the interaction of arsenious acid with bromic acid. The action of sulphuric acid is proportional to the square of the concentration of hydrogen-ions; the addition of neutral sulphates which reduce this concentration retards the reaction. The addition of hydrogen bromide causes the reaction to proceed in accordance with the formula $dx^1/dt=ka(b^1+x^1).(1-x^1)$, where b^1 is the concentration of the hydrobromic acid, x the initial concentration of bromic acid; the velocity constant remains the same. Hydriodic acid has a similar although much greater action, whilst the addition of chlorine-ions has a much smaller effect; from experiments in which neutral potassium halides were added it can be concluded that the relative accelerating effects of potassium chloride, bromide, and iodide are as 1 : 15 : 3,000. The addition of hydrogen chloride, owing to the simultaneous influence of both hydrogen- and chlorine-ions, has a much greater effect than that of sulphuric acid, whilst arsenic acid, which is the final product of the reaction, also acts as a positive catalyst, although nine times weaker than an equivalent quantity of sulphuric acid. The thermal coefficient of the reaction is normal and amounts to 2·14. G. A. R. K.

The Mechanism of Reduction. III. H. J. PRINS (*Rec. trav. chim.*, 1923, **42**, 942—953; cf. this vol., ii, 548).—In continuation of his previous work, the author has studied the influence of the structure and purity of zinc on the reduction of nitrobenzene in acetic acid solution. The action is practically independent of the

crystalline state of the metal, except in the case of the mechanically strained outer layer. At 53°, hydrogen is evolved during the reduction, with a velocity which is constant and independent of the reduction reaction, until about one-fourth of the surface of the metal becomes covered with reaction products.

The velocity of reduction is a linear function of the nitrobenzene concentration up to a critical value of the latter; in this region the surface of the metal remains bare. At higher concentrations a portion, θ, of the surface becomes covered with reaction products, and it is found that the equilibrium velocity is given by the equation $V_{eq}=K_1c(1-\theta)$, so that there can be no reaction on the covered part of the metal. It is supposed that the protective layer is zinc acetate adsorbed by the zinc. H. H.

Measurement and Calculation of Reaction Velocity. H. VON EULER and ERIK RUDBERG (*Z. anorg. Chem.*, 1923, **127**, 244—256; cf. A., 1922, i, 219, and ii, 40).—The influence of the concentration of hydrogen-ions on the velocity of hydrolysis of acetamide and of sucrose was studied. The first case was treated as a bimolecular reaction and the fall of hydrogen-ion concentration with time noted. Electrometric measurements with sulphuric acid and acetamide gave $K_b=3\times10^{-15}$ at the ordinary temperature, in good agreement with earlier values. An attempt was made, but unsuccessfully, by using sodium hydroxide, to measure K_a for acetamide.

Similarly, the effect of p_H on the hydrolysis of sucrose was studied, and it is pointed out that special precautions have to be taken with regard to absorption of carbon dioxide from the air or alkali from glass vessels, if the p_H lies above 4. In these cases, electrometric control is essential. From their results, the authors consider that sucrose has the dissociation constant $K_b=1\times10^{-19}$ or 10^{-20}, and they support Dushman's view (A., 1921, ii, 315) that $K=\nu e^{-h\nu/RT}$, where ν is a frequency probably associated with electrons within the molecule. H. H.

Kinetics of the Conversion of Creatine into Creatinine in Hydrochloric Acid Solutions. GRAHAM EDGAR and R. A. WAKEFIELD (*J. Amer. Chem. Soc.*, 1923, **45**, 2242—2245).—Measurements have been made of the rate of conversion of creatine into creatinine in hydrochloric acid solutions of concentrations 0·19*N*, 0·38*N*, and 0·76*N* at 25°, 57°, 78°, and 100°. The reaction is strictly unimolecular and the velocity increases with increasing concentration of acid. The temperature coefficient is given by Arrhenius's equation, in which the critical increment E has a mean value of 20,000 cal. and is independent of the acid concentration. The velocity constant can be expressed by the equations $\log_e K=-E/RT+C$ and $\log_{10}K=-4368/T+C^1$, where C and C^1 are constants depending on the concentration of the acid. J. F. S.

Catalytic Oxidation of Carbon Monoxide. I. Efficiency of the Catalysts Manganese Dioxide, Cupric Oxide, and Mixtures of these Oxides. J. A. ALMQUIST and WILLIAM C. BRAY (*J. Amer. Chem. Soc.*, 1923, **45**, 2305—2322).—Temperature-

efficiency curves have been obtained for three series of partly hydrated porous catalysts of manganese dioxide and cupric oxide. A very definite improvement in the efficiency is caused by the addition of a small amount of either oxide to the other. Partial dehydration is necessary to bring a catalyst to a region of maximum activity, but the water content may then be lowered to a relatively small value by slow dehydration with but little change in the efficiency. Continued dehydration, however, finally lowers the efficiency, and causes loss of oxygen (except in the case of copper oxide). The efficiency of a catalyst is independent of the carbon monoxide concentration between 0·1 and 0·6%, and is practically unchanged by the presence at higher concentration of carbon dioxide, the product of the reaction. Water vapour has a marked poisoning effect which is reversible. It is probable that under steady state conditions the oxygen content of a catalyst is practically constant whether the catalyst is operating at low or high efficiency. A catalyst is reduced when treated with carbon monoxide in the absence of oxygen at a temperature at which it would act as a catalyst. The activity of a mixed catalyst is permanently impaired by this reduction, even when much of the lost oxygen is restored on subsequent operation as a catalyst. An hypothesis of the mixture effect in this case is put forward. J. F. S.

Catalysis. XVIII. The Phenomenon of Induction. N. R. Dhar (*Z. anorg. Chem.*, 1923, **128**, 207—211).—A discussion of the results of Skrabal (A., 1915, ii, 533; 1922, ii, 488), the author, and others on the reactions between iodic acid and hydriodic and sulphurous acid. The latter may be resolved into two reactions, (1) the reduction to hydriodic acid, which is slow but much influenced by change of temperature, and (2) oxidation of the hydriodic acid so formed by iodic acid left unchanged, which is very quick, but only slightly influenced by temperature; the second reaction is, however, slowed down by the presence of hydrogen-ions due to the formation of sulphuric acid in the first reaction. The whole reaction is therefore autocatalytic. If arsenious acid is used in place of sulphurous acid, the reduction (1) is much slower and even more strongly influenced by temperature. With other reducing agents there is no induction period, iodine being continuously liberated.

The reaction between a thiosulphate and salts of antimony, silver, bismuth, etc., has now been studied, and found also to have an induction period, depending on the temperature and concentrations; probably there are two reactions involved here also, thiosulphuric acid being first transformed into hydrogen sulphide and tetrathionic acid.

In the hydrogenation of unsaturated organic compounds in presence of colloidal metals, it is suggested that reaction of the hydrogen with oxygen adsorbed or occluded in the metal induces the reduction of the organic body. Similarly the observation of Venkataramaih (*Nature*, 1920, **106**, 46) that permanganate is reduced when a mixture of hydrogen and oxygen is exploded over

it may be explained not by the formation of active hydrogen, but as a reaction induced by the reaction between the hydrogen and oxygen. S. I. L.

Catalysis. XIX. Photochemical Catalysis. A. K. SANYAL and N. R. DHAR (*Z. anorg. Chem.*, 1923, **128**, 212—217).—The reaction between mercuric chloride and ammonium oxalate in sunlight has been studied, and it is found that the velocity of reaction is independent of the concentration of the former, *i.e.*, the reaction is unimolecular, although in absence of light it is bimolecular (see Dhar, T., 1917, **111**, 750). With ferric chloride and ammonium oxalate, reaction is extremely slow in the dark, even on boiling, but proceeds normally at the ordinary temperature if the mixture has been exposed to light for a short time. Carbon dioxide retards both reactions. Iron salts exercise a strong positive catalytic effect on all reactions between oxalates and oxidising agents.

Many salts of lead, bismuth, and mercury are sensitive to tropical sunlight, darkening in colour; this effect is accelerated by foreign substances, especially those having the same anion as the salt employed. Halide salts of these metals show loss of the halogen after exposure, lead bromide losing 8—10% of its bromine after seventy-five hours' exposure.

Various mixtures of gases exposed to tropical sunlight react at the ordinary temperature. S. I. L.

Catalysis. XX. The Relation between the Order of a Reaction and its Temperature Coefficient. N. R. DHAR (*Z. anorg. Chem.*, 1923, **128**, 218—228).—The temperature coefficient diminishes with the order of reaction, being greatest for nil-molecular reactions, lower for unimolecular, and lower still for multimolecular reactions. Pseudo-unimolecular reactions are generally really bimolecular, and have moderately high temperature coefficients; the real and not the apparent order of reaction determines the temperature coefficient. S. I. L.

Catalysis. XXI. The Action of Neutral Salts. N. R. DHAR (*Z. anorg. Chem.*, 1923, **128**, 229—240).—The effect of various neutral salts on the reactions between (*a*) oxalic acid and chromic acid, (*b*) formic acid and chromic acid, (*c*) sodium formate and iodine, (*d*) sodium formate and mercuric chloride, and (*e*) sodium formate and silver nitrate has been studied. Some salts retard, others accelerate, the effect being specific for each salt, and more pronounced in dilute than in concentrated solutions; the order of reaction is not affected, nor is the temperature coefficient; the effect of the salt is not modified by change of temperature. S. I. L.

Catalytic Combination of Ethylene and Hydrogen in the Presence of Metallic Copper. II. Measurements of Reaction Velocity at 150°, 200°, and 250°. ROBERT N. PEASE (*J. Amer. Chem. Soc.*, 1923, **45**, 2235—2242; cf. this vol., ii, 472).—A continuation of previous work (*loc. cit.*). The velocity of combination of ethylene with hydrogen in the presence of copper has been determined at 150°, 200°, and 250°. The results show that in this range

of temperature the reaction is more nearly bimolecular than at lower temperatures, the combination at 0° is approximately unimolecular with respect to hydrogen, and is somewhat inhibited by excess of ethylene. The more nearly normal character of the reaction at the higher temperature is believed to be due to the fact that in these circumstances the reacting gases are not adsorbed to a measurable extent by the catalysts. The temperature coefficient of the velocity is much smaller at the higher temperatures, and decreases with increasing temperature. These facts are explained in a qualitative manner by taking into account the decrease of adsorption with increasing temperature and the normal increase in the velocity of the surface action. J. F. S.

Studies of Electrovalency. III. The Catalytic Activation of Molecules and the Reaction of Ethylene and Bromine. RONALD GEORGE WREYFORD NORRISH (T., 1923, 123, 3006—3018).

The Origin of the Chemical Elements. A. VON WEINBERG (*Z. angew. Chem.*, 1923, **36**, 525—529).—An account of Bohr's recent theory of the orbits of revolution of electrons in the atoms from Li=3 to U=92 is given. The 3rd, 4th, 5th, and 6th electrons (Li, Be, B, C) describe elongated ellipses, the figure in the last instance regaining the symmetry of a tetrahedron. On further addition of electrons, the latter in consequence of the forces now present describe circles within the figure and with 8 added electrons the completely symmetrical neon is obtained. Continuing, the 11th electron describes an ellipse related to the neon complex as the 3rd electron was related to the helium nucleus and period III of the periodic system is obtained. In period IV the 8 elements Sc to Ni are formed by addition of electrons to the inner orbit and then follows a series similar to that of the earlier periods, and similarly with series V. This theory does not attempt to afford an explanation of the origin of the different elements. In framing a theory of this process, it is necessary to assume a universe filled with hydrogen nuclei and electrons of mass $1{\cdot}649 \cdot 10^{-24}$ g. and $0{\cdot}8996 \cdot 10^{-27}$ g., respectively, and also to assume the validity of the ordinary conceptions of mechanics such as inertia and centrifugal force, also of the Coulomb conception of electrical charges. It is, however, doubtful whether the helium atom can properly be considered as made up of 4 hydrogen nuclei and 2 electrons, although the atomic weight relation 4 : 1·008 can be explained on Einstein's hypothesis by loss of energy in association. The author prefers to treat the helium nucleus as differing radically from other complex nuclei and develops a theory analysing the atoms of the different elements in terms of hydrogen and helium nuclei. Meitner's differentiation of the nuclei of radioactive elements into a central nucleus carrying the atomic charge and a neutral part is extended by him to all complex nuclei and the elements tabulated with the hydrogen and helium nuclei in the two parts shown separately. The nuclei in the neutral part are presumed to revolve around the central nucleus attended by their own electrons. Elements having odd atomic

numbers will necessarily include a hydrogen nucleus in the central nucleus. Isotopes differ only in the components of the neutral part, and hence their chemical properties which depend on the orbits of the electrons about the central nucleus are identical. The elements from which Rutherford removed hydrogen nuclei by bombardment with helium nuclei (B, N, F, Na, Al, and P) are the simpler atoms having hydrogen nuclei in the neutral part, so that, strictly speaking, he only effected the interconversion of isotopes. Such isotopes as those of chlorine in which one helium nucleus in the neutral part is replaced by two hydrogen nuclei, could not be generated from each other, which is in accordance with the constant composition of chlorine in nature. This theory leads to the conception of the origin of the elements, not by the random encounter of complex nuclei with electrons, but by the combination of hydrogen and helium atoms, of which some remain intact in the neutral part and others, completely ionised, join the central nucleus, their electrons adding themselves to the main swarm. The non-existence of elements above uranium is explained as follows. The higher the charge of the nucleus, the smaller is the diameter of the innermost electronic orbit, both on account of the increased attraction of the nucleus and the increased repulsion of the outer electrons. In the case of uranium, the radius of this orbit has fallen to the order of $1 \cdot 10^{-13}$, which is about the radius of the nucleus itself, so that more complicated systems could have no stable existence. This synthetic view of the origin of the elements, which is also supported by the evidence of ionisation of elements at very high temperatures, as in stellar spectra, affords a rational explanation of the existence of radioactive elements in the world to-day. C. I.

The Bohr Atom. J. D. MAIN SMITH (*Chemistry and Industry*, 1923, **42**, 1073—1078).—The author discusses briefly the inadequacy of Bohr's theory of atomic structure and electron valency in its application to the explanation of chemical phenomena, instancing and illustrating the inability of the theory to explain the structure or the existence of certain simple compounds, *e.g.*, carbon monoxide, and its failure to account for the chemical activities of elements. Whilst the theory is incapable of general application in chemistry, it is applicable to all cases where simple atomic ions are concerned. The postulates concerning atomic linking and the number of co-valencies associated with an atom, introduced by Sidgwick in his extension of the Bohr theory to co-ordination compounds (T., 1923, **123**, 725) are examined critically, and the author concludes that they scarcely furnish a sufficient basis on which a consistent explanation of chemical phenomena can be built. Thus the author contends that there is no evidence to support the assumption of the existence of co-valencies, and shows, inter alia, that nine of the fourteen elements from lithium to chlorine are not in accord as regards respective values of the maximum co-ordination numbers predicted by application of the second postulate. Co-ordination numbers greater than 8, contrary to Bohr's theory,

are rare in chemistry, and, where they do occur cannot be predicted by the postulate, which is regarded as being inconsistent with the fundamental feature of Bohr's theory, which determines the electronic path about the nucleus in terms of the principal and secondary quantum numbers. The resolution of the "actual number of electrons" attached to an atom into groups is admissible only when such number is equal to Bohr's ionic numbers; otherwise the groups have no necessary reality. The extended theory assigns an anomalous position to hydrogen, for it disposes two of the four co-valency electrons in orbits to which their quantum number does not relate. Difficulties attending the application of the co-valency postulate appear to originate in the assumption that two shared electrons can be simultaneously effective in two atomic structures. Shared electrons must react as if only one at a time were effective in any one quantum orbit, and provision must be made for a harmonic reaction between shared and unshared electrons having the same quantum number. J. S. G. T.

Application of the Adiabatic Hypothesis to the Model of Ortho-helium. OTTO HALPERN (*Z. Physik*, 1923, **18**, 344—351).—The author shows mathematically that Bohr's application of the adiabatic hypothesis (this vol., ii, 478) to the model of ortho-helium due to Landé, and comprising a coplanar system of electrons, is unjustifiable, and attributes to this misapplication the discrepancy between observed and calculated values of terms in the spectral series relating to ortho-helium. J. S. G. T.

An Explanation of the Theory of the Rotation of the Atomic Nucleus. IV. HERBERT HENSTOCK (*Chem. News*, 1923, **127**, 241—243, 259—260; cf. this vol., ii, 400, 477, 679).—The octet of the nitrogen atom is probably distorted as far as the number of electrons present will allow. Two such distorted atoms when placed in juxtaposition in such a manner that the nuclei are orientated at right angles to one another form a model of the nitrogen molecule. There are no free valencies, and since no cube face is opened up to form the triple bond, the molecule must be very stable. The shape of the positive nitrogen atom is identical with that of the distorted carbon atom in carbon monoxide. This similarity, and the equality of the number of electrons present in the two molecules, may account for the property which nitrogen has of absorbing energy when present in an explosive mixture of carbon monoxide and oxygen (Bone, Newitt, and Townsend, *Proc. Roy. Soc.*, 1923, [*A*], **103**, 205). Nitrous oxide appears as N⁝N⁚O, which explains its easy reduction to nitrogen and its non-formation of hyponitrous acid with water.

In the second paper the structures of the oxides of nitrogen are discussed from the point of view of the author's theory (this vol., ii, 400, 477, 679). E. H. R.

The Ion of the Hydrogen Molecule, according to the Quantum Theory. K. F. NIESSEN (*Arch. Néerland*, 1923, **7**, 12—59).—Considering the ion of the hydrogen molecule as constituted of an

electron moving about two positive nuclei permanently at rest, the author, following the analysis developed by Jacobi in the analogous case of motion about two centres of force, determines mathematically the electronic trajectories which are mechanically possible. From such paths are selected those which are stable and conform with stability of the nuclei in accordance with classical mechanics; these may be quantised in accordance with the ideas developed by Bohr and Sommerfeld. It is shown that when three quantum numbers are associated with the trajectories, symmetrical paths about the nuclei are alone stable. An ion executing such a path does not emit a rotation spectrum, and whether the motion be symmetrical or asymmetrical, no vibration spectrum is emitted.

J. S. G. T.

Quantum Theory of the Hydrogen Molecule. L. NORDHEIM (*Z. Physik*, 1923, **19**, 69—94; cf. A., 1922, ii, 703).—Employing the method developed by Born and Pauli for the calculation of perturbed motions and utilising the principles applicable to degenerate dynamical systems as determined by Born and Heisen (this vol., ii, 478) and by Nordheim, the author discusses analytically the motion of two electrons each moving about its respective associated positive nucleus—a model representing the neutral hydrogen molecule. In the first part of the analysis, the distance between the nuclei is considered to be so large that each electron may be conceived as describing a Keplerian ellipse about the appropriate nucleus. Under these conditions it is shown that ten configurations of the electronic orbits are possible. Five of these are ruled out by the consideration that the energy associated with them is positive, indicating repulsion between them and the nuclei. Two of the remaining five electronic configurations comprise coplanar circular orbits executed either in the same or opposite directions about their respective nuclei. Two others comprise orbits inclined respectively both at 60°, or one at 60° and one at 120°, to the line joining the nuclei, whilst the remaining configuration consists of electronic orbits executed in parallel planes perpendicular to the line joining the nuclei. The respective positions of the electrons in their respective orbits are given. A consideration of the stability of dynamical systems leads to the conclusion, in agreement with the result found by Kramers (this vol., ii, 312), that no model of the hydrogen molecule consisting of two identical atomic systems can be inherently stable. A consideration of the perturbations in the respective electronic orbits in the various configurations due to the proximity of the second nucleus—a factor taken into account in the latter part of the analysis—leads to the conclusion that whilst three of the five electronic configurations referred to suffer perturbations in such manner as still to yield inherently stable systems, these three do not conform with experimental results in the matter of nuclear distance and molecular energy of combination. The greatest agreement is found in the case of the Bohr-Debye model, constituting one of the five models, and comprising two coplanar circular

electronic orbits executed in the same direction by electrons having a relative phase difference of 180°. The remaining two models, which, regarded from the physical point of view, have most to commend them, are rejected, as the type of their electronic motions is entirely altered by perturbations prior to the establishment of equilibrium. J. S. G. T.

Radii of the Atoms of the Alkali Metal Vapours. S. H. ANDERSON (*Physical Rev.*, 1922, **20**, 260).—By assuming that the ionising potential is one-half of the potential of a point on the orbit of the valency electron, and that the distribution of the electrons in the kernel is that suggested by Bury (A., 1922, ii, 43) and Bohr (A., 1922, ii, 277), the radii of the valency electrons of the alkali metals are computed as follows: lithium, $1{\cdot}379 \times 10^{-8}$ cm.; sodium 1·80; potassium, 2·21; rubidium, 2·45; cæsium, 2·695. When plotted against the integral numbers 2, 3, 4, 5, and 6, these values are uniformly distributed about a straight line. On passing from one metal to the next higher in the periodic table, an extra electron shell is therefore added to the atomic structure, and the shells are evenly spaced. A. A. E.

The Radii of the Alkali- and Halogen-ions and of the Atoms of Inert Gases. WHEELER P. DAVEY (*Physical Rev.*, 1923, [ii], **22**, 211—230).—An analysis of the author's measurements (this vol., ii, 413) of the ionic distances in the lattices of the alkali halides leads to the following conclusions: (1) These ions are packed as if they were nearly spherical. (2) The heavier ions have packing radii which are nearly constant, *i.e.*, independent of the ions with which they are combined. (3) The radii of potassium-, rubidium-, and cæsium-ions are approximately equal to those of the negative ions with the same number of electrons, chlorine, bromine, and iodine, respectively. The approximation is the closer the greater the atomic number. Assuming that (1) and (2) hold rigidly, and that the radii of cæsium- and iodine-ions are equal, the radii of the ions ($\times 10^{-8}$ cm.) are computed to be as follows: cæsium and iodine, 1·974; rubidium, 1·679; bromine, 1·737; potassium, 1·548; chlorine, 1·589; sodium, 1·1 to 1·2; fluorine, 1·0 to 1·2. These values are in general agreement with those obtained by Landé, Richards, and Saha, but not by Bragg. If it is assumed that for each inert gas the radius is the mean of those for the alkali- and halogen-ions with the same number of electrons, the packing radii are computed to be as follows: xenon, 1·97; krypton, 1·71; argon, 1·57; neon, 1·15. These results are only 0 to 0·27 unit higher than those obtained by Rankine from viscosity measurements. Derived values for the "atomic volume per electron" are approximately constant for the inert gases except in the case of argon, where it is low. In a note, it is argued that Wyckoff's value of 1·081 Å. for the radius of the chlorine-ion (this vol., ii, 311) is actually that of the neutral atom of chlorine. A. A. E.

Theory of Residual Affinity and its Application to Organic Chemistry. I. The Fundamental Principles of the Theory. A. ORÉKHOV (*Rev. gén. Sci. pur. Appl.*, **34**, 264—270; from *Chem. Zentr.*, 1923, iii, 279).—The author discusses Werner's theories of reciprocal desaturation of valencies in relation to simple, double, and treble linkings. It is concluded that in long carbon chains the linkings are variable and that periodic changes in properties occur. G. W. R.

The Electronic Theory of Valency. II. Intra-molecular Ionisation in Organic Compounds. III. The Transmission of Chemical Affinity by Single Bonds. T. MARTIN LOWRY (*Phil. Mag.*, 1923, [vi], **46**, 964—976, 1013—1020).—II. In continuation of previous work (this vol., ii, 480), the author shows that the theory of intramolecular ionisation can be extended to organic compounds, if it be assumed that double bonds can assume a form in which one carbon atom carries eight *L*-electrons, and the other six only, one pair of electrons being shared. This type of double bond is thus constituted of one co-valency and one electro-valency. On this assumption, ethane, ethylene, and acetylene have the respective formulæ $\begin{matrix}CH_3\rightharpoonup CH_3\\ CH_3-CH_3\end{matrix}$, $\begin{matrix}\overset{+}{CH_2}\rightharpoonup\overset{-}{CH_2}\\ CH_2=CH_2\end{matrix}$, $\begin{matrix}\overset{+}{CH}=\overset{-}{CH}\\ CH\equiv CH\end{matrix}$, the barb, $\rightharpoonup$, denoting an electro-valency passing from the positively to the negatively charged atom. This extension of the theory brings the reactivity of organic compounds into line with the activity of inorganic ions and makes it possible to regard all chemical action as ultimately ionic in character. The resting forms of molecules are not necessarily identical with their ionised or reactive forms. It is probable that organic compounds may be divided into two groups according as the normal structure of the molecule is polar and therefore reactive, or is non-polar and must undergo isomeric change into a polar form before it can react. Thus zinc methyl, sodium ethoxide, and methylethylaniline oxide probably have permanently ionised structures. In general, a compound which requires "activating" by heat or a catalyst, etc., before it will react is probably in a non-polar condition. It is pointed out that the theory of mixed double bonds affords a new interpretation, which is supported by experimental evidence, of the phenomena of conjugation discussed by Thiele, and of other phenomena. The properties of "multipolar ions," *i.e.*, ions which in addition to the electrification required to give the net charge of the ion possess additional positive and negative charges, afford a new interpretation of the phenomenon of tautomerism, and explain the readiness with which tautomeric ions yield co-ordination-compounds.

III. The author examines whether the two mechanisms discussed in previous parts are adequate to explain all the facts in reference to the transmission of chemical affinity through chains of atoms, or whether an additional mechanism is required. The existence of an unexplained residue of facts necessitating an additional mechanism is regarded as unproved, and the work of Lapworth

(T., 1922, **121**, 416) and of Flürscheim (T., 1909, **95**, 718) is examined in this connexion. It is pointed out that the reactivity of the methyl group in ethyl crotonate agrees with the theory of polar double bonds. It cannot be used as a proof of the existence of polarised single bonds, as it is interpreted simply in terms of Thiele's theory of conjugation. The small fluctuations observed in the strengths of unsaturated acids as the double bond is moved along the chain may be attributed to steric influences, depending on the configuration of the chain rather than on a reversal of polarity in alternate atoms. The fact that amino-acids are sometimes stronger than the acids from which they are derived is attributed to the acylous character of the amino-group: this is usually masked by the direct neutralising action of the basic group. The special mechanism devised by Flürscheim to explain the apparent anomaly is therefore unnecessary. The author concludes that alternate polarities are characteristic of conjugated systems, and it is not yet proved that they can be developed in chains of single bonds, where both acylous and basylous groups produce effects of constant sign. J. S. G. T.

Co-ordination and Acidity. T. M. LOWRY (*Chemistry and Industry*, 1923, **42**, 1048—1052).—Hydrogen is unique in that its combination with other atoms can only be represented by a single type of valency. A naked proton cannot lead an isolated existence, but will probably attach itself to any octet which is not too fully occupied by other atoms. From this point of view, the water in aqueous hydrochloric acid functions as an acceptor of hydrogen-ions: $H_2O+HCl \rightleftharpoons \overset{+}{O}H_3+\overset{-}{Cl}$. It is now suggested that water may take a more active part in the ionisation of acids by combining with the anion to form a co-ordinated complex anion and expelling the hydrogen-ion in the same way as the chlorine-ions are successively expelled from the triammine $[CoCl_3,3NH_3]$ by molecules of ammonia, with eventual formation of $[Co,6NH_3]Cl_3$. The final stage in the ionisation of sulphuric acid might then be represented by $[SO_4,xH_2O]H_2$. This theory of the relation between hydration and ionisation accords with the hygroscopic character of strong acids. The theory may be regarded as an extension of Werner's theory of acids and bases. E. H. R.

The Polarisation of Double Bonds. A. LAPWORTH and R. ROBINSON (*Nature*, 1923, **112**, 722).—Thomson (this vol., ii, 682) suggests that in such a system as $Cl-+Ⓒ_1-+Ⓒ_2-+Ⓒ_3-+Ⓒ_4-+Ⓡ$ the existence of the electrostatic doublet between Cl and C_1 will cause electrons to crowd into C_1 from C_2 and into C_3 from C_4, bringing about an alternating condition in the chain. For the same reason, however, that electrons pass from C_2 into C_1, it would appear that they should also pass from C_3 into C_2, and the effect would then be continuous, although diminishing in degree along the chain. If it is held that electrons may pass from one carbon atom to another if these are joined by a double bond, but not if they are joined by a single bond, the acceptance

of Kekulé's benzene formula in its simplest form is necessary. Moreover, Thomson's method of deduction of the alternate effect leads in numerous cases to results which are negatived by experiment. In this connexion, the behaviour of vinyl chloride and that of the group $C_3=C_2-C_1=O$ are discussed. The classification of atoms as "chemically active" or "chemically inert," according as there is a defect or excess of electrons, respectively, is considered to be unsatisfactory, since both types appear to be reactive under the correct conditions. A. A. E.

A Useful Substitute for Ground Joints in Vacuum Technique. A. von Antropoff (*Ber.*, 1923, **56**, [*B*], 2137—2138).—The principle of the mercury seal is utilised, but a fusible mixture of colophony, turpentine, and linseed oil is used as seal and is allowed to set solid before use. This mixture has the advantage of transparency. If the contents of the vacuum vessel must not come in contact with this mixture, a mercury seal covered with the colophony mixture may be employed. H. H.

Apparatus for Absorbing and Washing Gases. K. Keller (*Chem. Ztg.*, 1923, **47**, 506).—The apparatus consists of a cylindrical tube, closed at the bottom and fitted with a rubber stopper; the inlet tube for the gas extends just below the stopper, whilst the exit tube reaches into the liquid contained in the lower part of the cylinder. The exit tube is provided with a bulb below the stopper, and a spiral tube extends from the side of this bulb to just below the surface of the liquid. The gas entering the apparatus is forced upwards through this spiral tube, carrying with it a quantity of the liquid; if any liquid reaches the bulb it passes downwards through the central part of the tube below the bulb, whilst the washed gas leaves the bulb through the upper part of the delivery tube. W. P. S.

Extraction Apparatus with Device for the Recovery of Solvent. Twisselmann (*Chem. Ztg.*, 1923, **47**, 506).—A plain cylindrical tube (similar to the body of a Soxhlet extractor, but without a siphon tube) contains the substance to be extracted. The top of this tube is connected with a vertical condenser by a tapped tube provided with a large bulb above the tap, and a side tube (for the vapour of the solvent) extends from below the tap to the lower part of the condenser. During the extraction, the tap is open so that the condensed solvent passes through the substance in the extraction tube and thence to the extraction flask; when the extraction is complete, the tap is turned and the condensed solvent is collected in the bulb above the tap. W. P. S.

The Filtration of Viscous Liquids. A. Gutbier and E. Sauer (*Z. anorg. Chem.*, 1923, **128**, 15—16).—For the filtration of highly viscous liquids, such as 10—20% glue solution, the so-called "cellulose filter" is particularly useful. The substance is obtainable in square tablets which must be broken up as small as possible and placed in a capacious flask with hot water, and shaken until a uniform pulp is obtained. As a support for the

filter, a perforated porcelain plate or Buchner funnel may be used, covered with copper or nickel wire-netting. The pulped filter material is poured quickly on to the support, sucked dry, and well pressed down. The cake formed on the support should be 2—3 cm. thick. E. H. R.

A Simple Lecture Experiment for Obtaining Neon and Helium from the Air and Demonstrating the Absorbent Power of Charcoal. A. VON ANTROPOFF (*Ber.*, 1923, **56**, [*B*], 2135—2137).—A tube containing well-dried coconut charcoal is fused on to a vacuum tube fitted with electrodes. The other end of the charcoal tube is drawn out into a long, fine capillary and sealed. An induction coil is connected to the vacuum tube and the charcoal plunged into liquid air. Very soon the tube becomes luminous and then again dark as the air is condensed in the charcoal. Then the capillary is broken and air allowed to stream slowly into the tube through the cooled charcoal. The other components are absorbed and the spectrum of neon and helium may be demonstrated. H. H.

Inorganic Chemistry.

The Presence of Chlorine in Synthetic Hydrochloric Acid. B. NEUMANN (*Z. angew. Chem.*, 1923, **36**, 529—531).—A calculation of the theoretical temperature developed by the combination of equivalent volumes of hydrogen and chlorine gives the figure of 2648°, at which the degree of dissociation of hydrogen and chlorine may be 2%; but as the gases combine again very rapidly on cooling, this cannot account for the occasional presence of free chlorine in synthetic hydrogen chloride. It is due to the dilution of the chlorine with air and the employment of insufficient hydrogen to satisfy both the chlorine and oxygen present. In this case, the relation $K=[H_2O]^2[Cl_2]^2/[HCl]^4[O_2]$ obtains, and the value of K at different temperatures has been experimentally determined, log k at 25° being=13·28, at 600°=0, at 1984°=−4·30, according to Treadwell. There are also the relations $K=(x/2[1-x])^4.1/p_{O_2}$, in which x is the relative proportion of chlorine mols. to hydrogen chloride mols. (Haber) and $\log k=6034/T-6{\cdot}972$ (Treadwell). From these, for a gas mixture of given composition (initial and final) the value of T, the temperature of reaction, can be calculated. Results are tabulated for chlorine–air mixtures of various compositions, the hydrogen in each case being the equivalent of the chlorine. With excessive dilution, the heat of reaction will be insufficient to carry the reaction on, and the conclusion is drawn that for combustible mixtures the chlorine content of the final gas mixture will range between 0·5% and 5%. C. I.

Absorption of Atmospheric Gases by Water. J. H. COSTE (*Analyst*, 1923, **48**, 433—435; cf. A., 1917, ii, 463; 1918, ii, 265).—A graph is given showing the volumes of oxygen and nitrogen at *N.T.P.* dissolved by 1 litre of water of any salinity from 0 to 20 g. of chloride-ions per kg. of water. W. P. S.

A Simplified Graphical Representation of the Yield and Concentration Afforded by Ozone Apparatus. HANS BECKER (*Wiss. Veröffentl. Siemens-Konzern*, 1923, **3**, 243—247).—The yield, A, in g. of ozone produced per kw. hour is shown to be related to the concentration c and the limiting concentration C of ozone produced, by the linear equation $A=A_0(1-c/C)$. Moreover, the energy employed, W_Rt, per cubic metre of oxygen treated is given by $W_Rt=c/A$. These two linear relations are plotted on a diagram employing rectangular co-ordinates, the former appearing as straight lines drawn with values of A and c as ordinates and abscissæ respectively, whilst the latter is represented by a series of straight lines radiating from the origin and inclined to the axis of ordinates at respective angles given by $\tan^{-1} c/A$. From the diagram, the concentration of ozone, the yield and power employed in an apparatus for producing ozone may be read off directly. J. S. G. T.

Behaviour of Rhombic Sulphur at High Temperatures and Pressures. H. ROSE and O. MÜGGE (*Nach. K. Ges. Wiss. Göttingen*, 1922, **10**, 105—107; from *Chem. Zentr.*, 1923, iii, 288).—The deformability and plasticity of rhombic sulphur are not appreciably increased by heating at temperatures up to 281° under pressures of 1,000 to 19,600 kg. per sq. cm. The data of Tammann up to 3,143 kg. per sq. cm. pressure and 190° were confirmed by the authors. At higher pressures, the fusion curve of rhombic sulphur rises. At 19,300 kg. per sq. cm. it has m. p. 263°. G. W. R.

The Formation of Sulphur by the Action of Sulphur Dioxide on the Sulphides of Calcium, Zinc, and Iron. LOTHAR WÖHLER, F. MARTIN, and E. SCHMIDT (*Z. anorg. Chem.*, 1923, **127**, 273—294).—Sulphur dioxide acts on calcium sulphide at temperatures below 1,000° to give the sulphate and sulphur, but the reaction is soon brought to a standstill owing to the formation of a protective layer of sulphate on the pieces of sulphide. By working at temperatures above 1,000°, this can be avoided, as the reaction products are lime and sulphur. The low temperature reaction can, however, be accelerated by the addition of triferric tetroxide, which acts as a catalyst. Zinc blende reacts with sulphur dioxide to give the oxide and sulphur, but here again the reaction velocity rapidly diminishes owing to the formation of a protective layer, in this case of basic sulphide. Both sulphides of iron react with sulphur dioxide to give triferric tetroxide and sulphur. The reaction is rapid and complete, being catalytically accelerated by the oxide. H. H.

Sulphurous Acid and its Salts. I. The Decomposition of Sulphurous Acid and its Salts in Aqueous Solution. F. FOERSTER, F. LANGE, O. DROSSBACH, and W. SEIDEL (*Z. anorg. Chem.*, 1923, **128**, 245—342).—The spontaneous decomposition of sulphurous acid, forming sulphuric acid and sulphur, proceeds extremely slowly, requiring at 100° several days and at 150° about two days for completion. The change is autocatalytic, being accelerated by the sulphur and retarded by hydrogen-ions; the latter effect masks the former as the change proceeds. Dilute solutions decompose more quickly and completely than concentrated solutions, whilst in acid solutions the decomposition is inhibited, being completely suppressed in $2N$-hydrochloric acid solution.

The first stages in the decomposition are probably (*b*) $2HSO_3' \longrightarrow SO_4''+SO+H_2O$, and (*c*) $2SO+H_2O \rightleftharpoons S_2O_3''+2H^{\cdot}$, (*b*) being extremely slow. The positive catalytic action of sulphur is probably due to the formation of thiosulphate, (*d*) $HSO_3'+S \rightleftharpoons S_2O_3''+H^{\cdot}$, which is very rapid in comparison with (*b*) and (*c*), and gives rise to penta-, tetra-, and tri-thionic acids, thus, (*e*) $5S_2O_3''+6H^{\cdot} \longrightarrow 2S_5O_6''+3H_2O$, (*f*) $S_5O_6''+HSO_3' \longrightarrow S_4O_6''+S_2O_3''+H^{\cdot}$, (*g*) $S_4O_6''+HSO_3' \longrightarrow S_3O_6''+S_2O_3''+H^{\cdot}$, and finally to sulphuric acid, (*h*) $S_3O_6''+H_2O \longrightarrow SO_4''+S_2O_3''+2H^{\cdot}$, all these changes (*e*) to (*h*), proceeding very rapidly in comparison with (*b*); the intermediate polythionic acids increase rapidly in the solution at the beginning. The thiosulphuric acid formed is, however, transformed back to sulphurous acid by hydrogen-ions, $S_2O_3''+H^{\cdot} \longrightarrow HSO_3'+S$, which reaction prevents the changes (*d*) to (*h*) and brings the decomposition to a halt.

The strong positive catalytic effect of hydriodic acid on the decomposition is ascribed to the formation of complex ions. The decomposition of the metal hydrogen sulphites is different from that of the acid itself in that until the decomposition is far advanced the concentration of hydrogen-ions remains low, being that of a hydrogen sulphite–sulphurous acid solution; the change is therefore very strongly positively autocatalytic, and is greatly hastened by addition of sulphur or polythionates. If sulphur dioxide is allowed to escape from the solution, as by boiling a strong sodium hydrogen sulphite solution in an open vessel, polythionic acids are not formed, the mechanism following (*b*) and (*c*) above being $S_2O_3''+H_2O \longrightarrow SO_4''+H_2S$, $S_2O_3+2H^{\cdot} \longrightarrow SO_2+S+H_2O$, and $2H_2S+SO_2=3S+2H_2O$.

Selenium and selenious acid act as powerful positive catalysts, forming the selenosulphuric-ion $SeSO_3''$ in the solution. Potassium selenosulphate and selenodithionate have been prepared in the pure state, and indications of the existence of selenium analogues of the polythionic acids obtained. The mechanism of the series of changes (*c*) to (*h*) when selenium dioxide is substituted for sulphur dioxide has been examined.

Tellurium when free from selenium has no catalytic activity with regard to the decomposition of hydrogen sulphites. S. I. L.

Preparation of Sulphuryl Chloride. SIR WILLIAM J. POPE (*Rec. trav. chim.*, 1923, **42**, 939—941; cf. T., 1920, **117**, 1410).—Bone charcoal or activated wood charcoal forms a most convenient

catalyst for promoting the union of sulphur dioxide and chlorine to form sulphuryl chloride. Combination occurs instantaneously, and, provided that the reaction vessel is cooled to 30°, the chloride is condensed and may be drained away as rapidly as it is formed. There seems to be no limit to the life of the catalyst. H. H.

The Alteration of Thiosulphate Solutions. F. Feigl (*Ber.*, 1923, **56**, [*B*], 2086—2088; cf. this vol., ii, 483, and A., 1922, ii, 873).—It is suggested that the alteration of thiosulphate solutions on keeping may be due to the decomposition of the thiosulphate into sulphate and sulphur which, under the influence of hydrogen-ions or of carbon dioxide, combine to form the co-ordination complex, $\begin{bmatrix} SO \\ S \\ OO \end{bmatrix} Na_2$. H. H.

The Preparation and Properties of Selenium Trioxide and Chloroselenic Acid. Richard Robert le Geyt Worsley and Herbert Brereton Baker (T., 1923, **123**, 2870—2875).

Ammoniates as Binary Systems. III. Water–Ammonia. Fritz Friedrichs (*Z. anorg. Chem.*, 1923, **127**, 228).—The author cannot confirm the existence of the two hydrates of ammonia described previously by Rupert (A., 1909, ii, 726). H. H.

The Catalytic Oxidation of Ammonia and Hydrogen Cyanide. I. Józef Zawadzki (*Roczniki Chemji*, 1923,* **11**, 145—157).—A full summary is given of the work published on the subject by different authors and the results are compared and criticised. G. A. R. K.

The Catalytic Oxidation of Ammonia and Hydrogen Cyanide. II. Józef Zawadzki and Jan Wolmer (*Roczniki Chemji*, 1923, **2**, 158—182).—The oxidation of ammonia and hydrogen cyanide was carried out in an electrically heated quartz tube containing platinum or ferric oxide as a catalyst, using concentrated sulphuric acid to absorb the products of the reaction.

Most of the experiments with ammonia were carried out with a platinum catalyst in the form of gauze (400 per sq. cm.); the ferric oxide catalyst did not give good results. The effect of different temperatures, rates of flow of gas, and partial pressures of ammonia were studied, and the results are expressed in the form of curves. These show that at temperatures below 750° the yield of oxides of nitrogen increases with an increase in the rate of flow, that is, with a shortening of the time of contact between the reacting gases and the catalyst; the increase in yield reaches a maximum and then diminishes (for rates of flow from 2 to 42 litres per hour), but at temperatures above 750° the increase is continuous. It is also found that the greater the rate of flow the higher the optimum temperature of the reaction. There seems to be no absolute optimum temperature for this reaction; a short contact with the catalyst and a high temperature appear to be the most favourable conditions. The effect of the partial pressure of ammonia

in the reaction mixture is not very great. The relative amounts of nitric oxide and nitric peroxide formed depend entirely on the extent to which the nitric oxide in the reaction product undergoes oxidation.

The experiments with hydrogen cyanide in the presence of ferric oxide show that the yield of oxides of nitrogen increases with increase of temperature up to 780°; the rate of flow of the reaction mixture is of secondary importance; a few experiments carried out with the platinum catalyst mentioned above show that the yields are comparable with those obtained in the oxidation of ammonia under similar conditions, and an increase in the rate of flow of the gases is beneficial at high temperatures.

The mechanism of the catalytic oxidation of ammonia is discussed, and it is suggested that the first step is the dissociation of the ammonia into its constituent elements; the atomic nitrogen then combines with oxygen to form nitric oxide, provided the temperature is not too high to allow the existence of this compound; otherwise the reaction $N+N=N_2$ will proceed at the expense of the reaction $N+O=NO$, and it is on the relative rates of these two reactions that the yield of the desired product depends. The view put forward by Neumann and Rose (A., 1920, ii, 247) that the formation of nitrogen at higher temperatures is due to the direct oxidation of the ammonia to nitrogen and water is criticised, because in that case the reaction should be independent of the rate of flow of the gases and show a definite optimum temperature, whereas it is now shown that equally good results can be obtained with higher temperatures than those used by Neumann and Rose (500°), provided the flow is suitably accelerated. It is also shown that nitric oxide decomposes quite appreciably (12·2 % at 800°) under conditions similar to those used, and this decomposition is greatly assisted by contact with a platinum catalyst.

The reason of the poor yields at temperatures below 500° may perhaps be attributable to the reaction between ammonia and nitrogen trioxide and peroxide, whilst at higher temperatures these oxides dissociate into oxygen and nitric oxide. G. A. R. K.

Action of Sulphur Chloride on Ammonia, and on Organic Bases. ALEXANDER KILLEN MACBETH and HUGH GRAHAM (*Proc. Roy. Irish Acad.*, 1923, **36**, 31—40).—By adding an ice-cold chloroform solution of ammonia to sulphur monochloride in the same solvent, nitrogen sulphide is obtained according to the equation: $12SCl+16NH_3=N_4S_4+12NH_4Cl+4S_2$. Other sulphides of nitrogen, however, are formed, for after precipitation of the sulphide, N_4S_4, by the addition of alcohol, the mother-liquors may be concentrated to obtain nitrogen pentasulphide, N_2S_5, and also *hexasulphamide*, S_6NH_2, which crystallises in colourless, square plates, m. p. 105°, insoluble in water, but soluble in organic solvents. This compound gives a coloration with alcoholic potassium hydroxide and with alcoholic solutions of organic bases. It is thought that this coloration may be due to the formation of a salt of a nitrogen-sulphur acid, but attempts to obtain such an acid or its salts were unsuccessful. H. H.

Ammoniates as Binary Systems. II. Hydrazine-Ammonia. FRITZ FRIEDRICHS (*Z. anorg. Chem.*, 1923, **127**, 221—227; cf. A., 1921, ii, 503).—Carefully purified hydrazine has m. p. $+1\cdot8°$, as determined by a dilatometric method. The three-dimensional pressure-temperature-concentration diagram for the system hydrazine-ammonia has been completely mapped out, and it is shown that no compound of the two components is formed.

H. H.

The Atomic Weight of Boron. ALFRED STOCK and ERNST KUSS (*Z. anorg. Chem.*, 1923, **128**, 49—75).—The accepted atomic weight of boron, 10·90, is probably too high. According to Aston, boron contains two isotopes of atomic weights 10 and 11, in such proportions that the experimental atomic weight should be about $10\cdot75\pm0\cdot07$. Baxter and Scott have recently found $10\cdot83\pm0\cdot01$ by analysis of the chloride and bromide (A., 1922, ii, 285), and Hönigschmid and Birckenbach (this vol., ii, 559) adopt the value 10·82, also from the chloride. The authors have now made use of the gaseous boron hydride, B_2H_6, for the atomic weight determination, by measuring the volume of hydrogen formed by reaction of a known weight of the gas with water: $B_2H_6+6H_2O=2H_3BO_3+6H_2$. This reaction is shown to proceed quantitatively. The hydride, B_2H_6, was prepared by heating B_4H_{10} to 95° for five hours, followed by fractional distillation at low temperatures. As a result of six concordant experiments, the atomic weight of boron is found to be $10\cdot8055\pm0\cdot0015$. This is the lowest value so far obtained.

The atomic weight of silicon was determined in a similar manner, using the reaction of silicon hydride, with sodium hydroxide: $SiH_4+2NaOH=Na_2SiO_3+4H_2$. This work was carried out before the methods of precision finally adopted in the work on boron had been fully developed. Three closely agreeing experiments gave the mean atomic weight for silicon 28·15, which is considerably lower than the accepted value (28·3).

E. H. R.

The Coefficients of Viscosity and Slip of Carbon Dioxide by the Oil Drop Method, and the Law of Motion of an Oil Drop in Carbon Dioxide, Oxygen, and Helium at Low Pressures. JAMES M. EGLIN (*Physical Rev.*, 1923, **22**, 161—170).—The coefficient of viscosity of carbon dioxide, determined by the oil drop method, is $1\cdot478\times10^{-4}$ at 23° and 760 mm.

A. A. E.

The Interaction of Potassium Tetroxide with Ice and with Dilute Sulphuric Acid. HERBERT HAWLEY and HENRY JULIUS SALOMON SAND (T., 1923, **123**, 2891—2896).

A Study of Secondary Valency by Means of *X*-Rays. GEORGE L. CLARK and WILLIAM DUANE (*Physical Rev.*, 1922, **20**, 85—86; cf. A., 1922, ii, 483).—Potassium tri-iodide, preserved against sensible decomposition, was analysed by the *X*-ray method and found to be centred cubic, with an iodine atom going to the centre of each of the original unit cubes of potassium iodide, thereby increasing

the edge length from 3·532 to 4·680 × 10^{-8} cm. The number of molecules per unit cube was found experimentally to be 0·4986.

A. A. E.

Promoter Action in the Decomposition of Potassium Chlorate. HARVEY A. NEVILLE (*J. Amer. Chem. Soc.*, 1923, **45**, 2330—2333).—The fact that commercial manganese dioxide is a more effective catalyst in the decomposition of potassium chlorate than the pure material is shown to be due to the presence of 8·8% of ferric oxide in the commercial article. Experiments with mixtures of these two oxides confirm this view, and show that each oxide is a promoter of the other. The action of cupric oxide and manganese dioxide as mutual promoters is also shown experimentally. J. F. S.

The Melting-point (Solidus) Curve for Mixtures of Potassium Nitrate and Sodium Nitrate. WALTER MATTHEW MADGIN and HENRY VINCENT AIRD BRISCOE (T., 1923, **123**, 2914—2916).

The Structure of Crystals of Sodium Bromate and Sodium Chlorate. L. VÉGARD (*Z. Physik*, 1923, **18**, 379—381).—The author replies to criticism by Kolkmeijer, Bijvoet, and Karssen (this vol., ii, 414) of the structures attributed by him to crystals of sodium bromate and sodium chlorate. Considerations of the relative numbers and intensities of lines in the respective *X*-ray spectra, and of the experimental determination of these intensities lead the author to conclude that the structures proposed by him are to be preferred to those suggested by his critics. J. S. G. T.

Investigation with X-Rays of the Structure of Crystals of Sodium Chlorate and Sodium Bromate. A. KARSSEN (*Rec. trav. chim.*, 1923, **42**, 904—930).—An attempt to decide between the models proposed by the author and others (A., 1921, ii, 200) and those proposed by Dickinson and Goodhue (A., 1922, ii, 145). It is concluded that with the present uncertain underlying assumptions no final choice can be made. H. H.

Heterogeneous Equilibria in the Ternary System Sodium Sulphite–Sodium Sulphate–Water. ALBERT CHERBURY DAVID RIVETT and NEIL BANNATYNE LEWIS (*Rec. trav. chim.*, 1923, **42**, 954—963).—Isotherms in the ternary system sodium sulphate–sodium sulphite–water were obtained at 0·1°, 17·5°, 25°, and 37·5°. The stable systems at the three lower temperatures show two series of mixed crystals, one between the heptahydrates, and one between the decahydrates of the salts. At 25°, there is also a metastable system of mixed crystals of the anhydrous salts. At 37·5°, the stable system is one in which there are three series of mixed crystals between the anhydrous salts. H. H.

X-Ray Investigation of the Crystal Structure of Lithium and Lithium Hydride. J. M. BIJVOET (*Rec. trav. chim.*, 1923, **42**, 859—903).—The elementary cell of lithium is found to be a centred cube with an edge of 3·50 Å., each cell containing two atoms: the "atomic domain" is 3·04 Å. in diameter. A lattice of stationary valency electrons does not explain the results obtained,

and it is thought possible that the valency electron rotates round the nucleus, or possibly between the nuclei, in planes perpendicular to the trigonal axes.

Lithium hydride also crystallises in cubes with four LiH groups per unit cell of side 4·10 Å. Two models appear to fit the facts: (*a*) with atoms at the points of the lattice with radii of the same order of magnitude as found by Bohr for the free atoms: (*b*) with positive lithium-ions and negative hydrogen-ions at the points of the lattice, the electrons rotating round the nuclei in planes perpendicular to the non-intersecting trigonal axis. In this case, the radius of the lithium$^+$-ion is about 0·05*a*, and of the H^--ion is about 0·58*a*. This structure, of course, implies a heteropolar binding in the hydride, as against a homopolar linking in the metal. H. H.

Crystal Structures of Lithium Iodide and Rubidium Fluoride. R. W. G. WYCKOFF and EUGEN W. POSNJAK (*J. Washington Acad. Sci.*, 1923, **13**, 393—397).—An apparent discrepancy in the results obtained by the authors (A., 1922, ii, 214, 499) and by Davey (this vol., ii, 413) for the crystal structure of lithium fluoride as determined by *X*-ray analysis, is attributed to the probability that the material employed by the latter was not the anhydrous salt. Additional *X*-ray data referring to lithium iodide are given. It is pointed out that the observed intensities of the diffraction lines obtained with the material used are different from those calculated for the assigned structure, and that the calculated interatomic distances associated with this structure do not agree with those to be anticipated from a consideration of "atomic radii" determined by W. L. Bragg (A., 1920, ii, 537). The structure of lithium iodide, as determined by the authors from observations on the fused material, gives a "sodium chloride arrangement" of the atoms for which the atomic distance, Li to I, is in substantial agreement with that to be anticipated from the additive rule, viz., 3·015 Å. Accepting this structure, the only outstanding discrepancy between calculated and anticipated values of atomic distances amongst the alkali halides would be that associated with the crystal structure of rubidium fluoride, additional data for which are given. J. S. G. T.

Aqueous Solutions of Ammonium Hydrogen Carbonate. CLAUDE BONNIER (*Compt. rend.*, 1923, **177**, 685—688).—A study of the effect, on the gaseous pressure produced in closed vessels, by aqueous solutions of ammonium hydrogen carbonate, of (1) the concentration of the solution, and (2) the relation between the volumes of liquid and gaseous phases (cf., also, Dibbits, A., 1875, 421, and Berthelot and André, A., 1887, 11). The results are expressed by means of curves, which should be consulted for details. E. E. T.

Rendering Thin Silver Films on Glass Visible. J. ESTERMANN and O. STERN (*Z. physikal. Chem.*, 1923, **106**, 399—402).—Gerlach and Stern have shown previously that invisible silver films may be rendered visible by physical development (*Z. Physik*,

1921, **8**, 110; 1922, **9**, 349, 353). The present paper deals with experiments designed to ascertain the minimum thickness of silver which can be detected in this manner. The silver films were produced from a silver-plated platinum wire which on heating emits a stream of silver atoms; these pass through a small hole in a platinum screen and on to the glass. The thickness of the film may be calculated by the formula $d=d_0.\rho^2/r^2$, where d_0 is the thickness of the silver on the platinum wire, ρ the radius of the hole in the screen, r the distance of the screen from the glass plate, and d the thickness of the film. The plate of glass after exposure is placed in a solution of 1—2% quinol containing a little gum arabic and then 1—2 drops of 1% silver nitrate are added. After a few minutes, the film commences to show. It is shown that the thinnest film detectable by this method is 2×10^{-9} cm. Holding the film in cadmium vapour also develops it, the limit of the method being the same as above. Experiments with copper films produced in the same manner show that a film of this metal of the same thickness as the silver can be detected by the same method. J. F. S.

Structure of Thin Silver Precipitates. J. Estermann (*Z. physikal. Chem.*, 1923, **106**, 403—406).—In an earlier paper (preceding abstract) a method is described whereby thin silver films were rendered visible by a physical development which consisted in depositing silver or cadmium on the film. It is now shown that the developed film in some cases could be removed as a foil, but in others it remained as mere spots of silver of a grey or brown colour. The silver films have therefore been examined ultramicroscopically. It is shown that films 3×10^{-9} cm. thick are made up of definite individual particles. Since an ultramicroscopic particle must consist of at least 1,000 atoms, it follows that these crystals cannot be formed from silver deposited in the position where the crystal is found. It is suggested that the silver atoms are adsorbed on the glass and that by collisions with other atoms in the adsorption layer the crystals are built up. The author's experiments indicate that the mean free path of the silver atoms is of the order of 100 atomic diameters. J. F. S.

Reduction of Silver Salts by Means of Manganous Salts. Giuseppe Barberi (*Gazzetta*, 1923, **53**, 645—648).—The black, pulverulent precipitate formed on addition of 0·1*N*-ammoniacal silver nitrate solution to 0·1*N*-manganous sulphate solution at the ordinary temperature consists of a mixture of manganese dioxide and silver (cf. Wöhler, *Annalen*, 1837, **41**, 344). If the former solution contains only sufficient ammonia to dissolve the silver hydroxide first formed, the precipitate will have the composition MnO_2+2Ag. Rose's statement that the compound Mn_2O_3,Ag_4O is formed under these conditions (*Annalen*, 1857, **101**, 229) is erroneous. T. H. P.

The Action of an Aqueous Solution of Sodium Hyposulphite (Hydrosulphite) on Silver Chloride. The Recovery of Silver from Silver Chloride Residues. J. B. Firth and J. Higson (*J. Soc. Chem. Ind.*, 1923, **42**, 427—429T).—Solid silver chloride is

acted on to a small extent by dilute solutions (2—6%) of sodium hyposulphite. Stronger solutions (12—24%) are more active, the action increasing with rising temperature up to about 50°, then falling off at still higher temperatures, probably on account of decomposition of the hyposulphite. Under the most favourable conditions, using a 24% solution at 50°, the product consists of 10·05% unchanged silver chloride, 88·92% of silver, and 1·95% of sulphur (as Ag_2S). The product is therefore a mixture of silver and silver sulphide. A solution of silver chloride in sodium thiosulphate is immediately reduced in the cold by sodium hyposulphite to silver sulphide, whilst an ammoniacal solution of silver chloride is reduced quantitatively to metallic silver. These two reactions can be applied for the recovery of silver from silver chloride residues. E. H. R.

Transference of the Acid Radicle in the Solid Phase. II. J. ARVID HEDVALL and JOSEF HEUBERGER (*Z. anorg. Chem.*, 1923, **128**, 1—14).—The displacement of a basic oxide from a salt by a more basic oxide, as observed in the case of carbonates when they are heated with an oxide more basic than that present in the salt (A., 1922, ii, 766) has now been found to occur with sulphates. The sulphates examined included those of strontium, calcium, magnesium, zinc, copper, cobalt, and iron (Fe'' and Fe''') and the oxides used were those of barium, strontium, calcium, and magnesium. Reaction between the salt and oxide was detected from the heating curve. The reaction temperature was lowest with barium oxide, varying from 328—370° with different salts; with strontium oxide, it varied from 410—451°, and with calcium oxide from 516—584°, except in one case, with ferrous sulphate, when it was as low as 444°. Magnesium oxide required the highest temperatures as a rule, and these are not determinable with so high a degree of accuracy as in the other cases on account of the low heats of reaction. In all the cases observed, reaction occurs at a temperature much below the decomposition temperature of the salt. Reaction can only occur when the heat of reaction is positive, and is not reversible. The extent to which the reaction proceeds was determined in the case of copper sulphate. Using molecular proportions, with BaO, 12·2% remained unchanged, with SrO, 11·8%, and with CaO, 38·9%. When the proportion of oxide was increased, the proportion of copper sulphate left unchanged was correspondingly diminished. The reaction is to be regarded as a true solid phase reaction between space lattices in contact at a suitable temperature. E. H. R.

The Crystal Structure of Strontium Selenide. MABEL K. SLATTERY (*Physical Rev.*, 1922, **20**, 84).—Strontium selenide, prepared by heating the selenate to redness in a current of hydrogen, was examined by the powder method. The unit structure is a cube of dimensions 3·10 Å., the alternate corners being occupied by strontium- and selenium-ions. A. A. E.

Action of Barium Chloride on Sulphate in Fused Salts. HOWARD E. BATSFORD (*Ind. Eng. Chem.*, 1923, **15**, 1044).—If a

small proportion of barium chloride is added to a fused mixture of sodium and calcium chlorides, any sulphate present as impurity is quantitatively precipitated and the freezing point of the fused mixture is unaltered. C. I.

Quantitative Decomposition of Natural Fluorspar by Fusion with Excess of Sodium Carbonate. C. C. PALIT (*Z. anorg. Chem.*, 1923, **128**, 350—354).—Whilst freshly precipitated calcium fluoride is completely decomposed by the carbonate fusion within two hours, it was found that one fusion left a quantity of mineral fluorspar undecomposed, the amount so left varying with the degree of fineness of the pulverised mineral, the amount of sodium carbonate used, and the duration of the fusion. The residue from a single fusion of fluorspar was never less than 5·8% of the weight taken, but this residue may be completely decomposed by a second fusion with sodium carbonate. S. I. L.

The Vapour Pressure of Cadmium and its Alloys with Zinc. ALFRED CHARLES EGERTON and FRANK VICTOR RALEIGH (T., 1923, **123**, 3024—3032).

Constitution and Evolution of Oxides and Metallic Hydroxides. PAUL PASCAL (*Compt. rend.*, 1923, **177**, 765—768).—The measurement of specific magnetic susceptibility allows a clear distinction to be made between water present as (1) hydroxyl or (2) solvent of crystallisation, etc. In this way, the dehydration of various hydroxides has been studied. Cadmium hydroxide, when heated, passes irreversibly into the oxide, magnesium hydroxide, however, undergoing the corresponding change reversibly. In the case of zinc hydroxide, although dehydration is irreversible, water lost by the hydroxide is partly adsorbed by the oxide. Magnetic analysis enables these changes to be followed clearly, whereas they would not be detected by ordinary methods. Whilst zinc hydroxide, on drying at 160°, is partly converted into oxide, the latter, if resulting from the dehydration of the hydroxide at 205°, still retains 2—3% of water. E. E. T.

Cadmium Sulphide and the Estimation of Cadmium. ALFRED CHARLES EGERTON and FRANK VICTOR RALEIGH (T., 1923, **123**, 3019—3024).

The Isotopes of Lead. A. S. RUSSELL (*Nature*, 1923, **112**, 619—620).—The author's analysis of the complexity of elements (this vol., ii, 748) leads to the somewhat surprising conclusion that common lead consists principally of mass-numbers 204, 205, 206, 207, 208, and 210, of which probably 206 and 208 are the chief. Of these isotopes, 206, 208, 210, and possibly 207 are end-products of radioactive series; consequently this analysis, if confirmed experimentally, can of itself neither confirm nor support the view that common lead may be of radioactive origin. The odd mass-number 205 may possibly be an isobare. Minor additions to and corrections of previous results are given. A. A. E.

Adsorption of Gases by Copper. Robert N. Pease (*J. Amer. Chem. Soc.*, 1923, **45**, 2296—2305).—The adsorption isotherms of hydrogen, ethylene, ethane, carbon monoxide, and nitrogen at 0° and up to one atmosphere pressure have been determined. The results are discussed and the specific character of the adsorption is pointed out. The effect of poisoning the copper with mercury on the adsorption of hydrogen, ethylene, and carbon monoxide and also of partly deactivating copper, by heating, on the adsorption of hydrogen and ethylene, has been ascertained. In both cases, it has been found that the strong adsorption at low pressures has been markedly decreased whilst the additional adsorption at higher pressures has been little affected. From these results and certain incidental observations, it is concluded that the adsorption is due to specific adsorbing centres on the copper surface rather than to the copper surface as a whole. These centres, it seems reasonable to suppose, are regions of high curvature, or "peaks," on the surface. J. F. S.

Metallic Cementation. H. Weiss (*Ann. Chim.*, 1923, [ix], **20**, 131—195; cf. this vol., ii, 678).—The rate at which alloys, initially not in equilibrium, attain homogeneity was studied in the cases of copper-tin, silver-antimony, and copper-arsenic, the last-mentioned being in the form of a prehistoric axe containing 1·25% of arsenic. The results obtained may be adequately expressed as an exponential function of the absolute temperature and for the temperature range covered by experiment by $v=I/\theta=K\alpha^T$, where θ is time, T absolute temperature and K and α are constants (cf. Tammann and Schönert, A., 1922, ii, 772). The author is of opinion that his experiments do not distinguish clearly between the influence of temperature and that of concentration, but that the latter appears to be one of the controlling factors in those temperature regions in which cementation occurs in practice. No tendency to the attainment of homogeneity could be observed initially in the prehistoric specimen, but a more delicate experimental method is required in order to justify extrapolation of results to include phenomena occurring at the ordinary temperature. The various causes which may impair the accuracy of the experimental work are discussed, together with their bearing on the results which might be obtained by extrapolation, and it is shown that a possible interpretation would indicate the cessation of penetration on reduction of the temperature to 280°. Five alloys (silver-antimony, copper-antimony, silver-tin, gold-antimony, gold-lead) in which penetration occurs in the form of propagation of a chemical reaction were studied from the point of view of the time factor, and the general conclusion drawn is embodied in the equation $\theta=mx+n/2.x^2$. As the time taken by the chemical reaction is negligible in comparison with that required for penetration, mx may be omitted and θ becomes $n/2.x^2$, where $n/2$ is the time required for formation of a homogeneous layer 1 mm. in thickness and x the thickness of the layer formed. The propagation of a zone of given concentration is thus proportional to the

square root of the time if the conditions remain unchanged. The size of the crystals formed and the possibility of the existence of regions which differ in stability may affect the results obtained. The author states that he does not claim to have thrown light on the mechanism of penetration, but the results show that the phenomena observed appear to become capricious as the temperature decreases. A few observations, admittedly incomplete, on the mutual penetration of crystalline salts were made. H. J. E.

The Equilibrium Diagram of the System Cuprous Sulphide–Ferrous Sulphide. C. B. CARPENTER and C. R. HAYWARD (*Eng. Mining J. Press*, 1923, **115**, 1055—1061).—The diagram is of the type obtained when the two components of the system are completely soluble in each other when liquid, but only partly so when solid. The two branches of the curve intersect at the eutectic point (995°, 68% FeS). Solid solutions are formed with limits of solubility at 92·5% FeS and 50% Cu_2S, respectively; compounds are not formed. Ferrous sulphide has f. p. 1163°, and cuprous sulphide has f. p. 1,128°. A transformation occurs in the solid state at 950°, due probably to a dimorphic change in the crystal habit of cuprous sulphide. In the range 15—45% FeS, if the mass is heated considerably above its melting point, loss of sulphur by volatilisation, and consequent interaction of iron with cuprous sulphide, leads to the separation of copper. A matte of 32% Cu (60% FeS) gradually lost sulphur when maintained at 1,100°. Photomicrographs are given, and the experimental procedure is described. CHEMICAL ABSTRACTS.

Separation of the Rare Earths by Basic Precipitation. V. Preparation of Cerium-, Lanthanum-, and Coloured Earths from Thorium-free Monazite Sand. WILHELM PRANDTL and JOSEPH LÖSCH (*Z. anorg. Chem.*, 1923, **127**, 209—214; cf. A., 1922, ii, 769).—The crude sand is dissolved in concentrated nitric acid and potassium bromate solution added to precipitate the cerium. The filtrates are concentrated, and this process is repeated until all the cerium is removed. The coloured earths (samarium, neodymium, and praseodymium) are then fractionally precipitated by the addition of ammonium and cadmium nitrates. The lanthanum appears in the final precipitates.

H. H.

Double Carbonates of Sodium and Metals of the Cerium Group. F. ZAMBONINI and G. CAROBBI (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 125—130).—Contrary to the statement of Meyer (A., 1904, ii, 734), these double carbonates are easily obtained crystalline and have the general formula $M_2(CO_3)_3,Na_2CO_3,12H_2O$. The lanthanum sodium compound forms microscopic spherolites which, left in the mother-liquor, change either to slender, microscopic needles, mostly united in parallel bundles, or to irregular lamellar aggregates. The cerium sodium compound forms minute spherolites changing, in the mother-liquor, to bundles of needles and lamellar aggregates. The praseodymium sodium compound

forms either pale green complicated aggregates resembling minute lamellæ or bundles of needles. The neodymium sodium compound forms aggregates of needles. The samarium sodium compound, $SmNa(CO_3)_2,6H_2O$ (Cleve, A., 1885, 636, gave $8H_2O$), forms characteristic minute rosettes. T. H. P.

The Crystal Structure of Mercury. L. W. McKeehan and P. P. Cioffi (*Physical Rev.*, 1922, **19**, 444—446).—Hull's powder method was employed in connexion with a thin coat of minute mercury droplets condensed on the outer surface of a paraffin- or shellac-coated rotating glass capillary tube, the mercury being maintained at about −115° by the vapour from boiling liquid air. The lattice appears to be rhombohedral, with the axial ratio 1·94. The calculated density, if one atom is associated with each cell, is 13·97 g./cm.^{3}; that computed from Mallet's and Dewar's results is 14·29 g./cm.^{3}. The disparity may indicate that a closer packing of atoms can occur in large ingots than in microscopic droplets. A. A. E.

Dynamic Allotropy of Mercuric Iodide. A. Damiens (*Compt. rend.*, 1923, **177**, 816—818).—It is shown that Smits's theory of dynamic allotropy (cf. A., 1915, ii, 262, and A., 1917, ii, 174), as applied to mercuric iodide, is contradictory to the law of the displacement of equilibrium, and that the results of his experiments on the rapid cooling of heated mercuric iodide are incomplete. According to Smits, the speed of reconversion (into the red variety) of yellow mercuric iodide, heated at temperatures above the transition point (127°), and subsequently cooled in liquid air, is greater the higher the temperature of heating. Whilst this is now confirmed for a first heating and cooling of commercial or precipitated iodide, it is not confirmed for a second or third heating and cooling; with well-developed crystals of the iodide, or with a sample that has previously been fused, reconversion to the red form takes place instantaneously on cooling, independently of the temperature of heating, even where this is as low as 135°. Smits's results are readily explained; the higher the temperature at which heating of microcrystalline iodide is effected, the higher the percentage of large crystals in a sample, owing to increased sublimation, and hence the accelerated recovery on cooling. E. E. T.

Mechanism of the Reduction of Permanganate and its Physico-chemical Basis. VI. Mangani-manganate as an Intermediate Product of the Reduction of Manganate. Josef Holluta (*Z. physikal. Chem.*, 1923, **106**, 324—340; cf. A., 1922, ii, 771, this vol., ii, 744).—The absorption spectra of manganate and mangani-manganate have been investigated and it is found that absorption spectra of these two substances differ sufficiently for the measurement of the spectrum of a strong alkaline solution of these substances to indicate their presence or absence from a reaction mixture. It is shown to be likely that the measurements of the absorption spectrum of manganate made hitherto have been effected with solutions containing also mangani-manganate. The

course of the reduction of manganate in strongly alkaline solution has been investigated, and it is found that in solutions which are $4 \cdot 0N$ with respect to alkali an intermediate compound is formed, the bright blue solutions of which give a similar absorption spectrum to that given by mangani-manganate described by Auger and Billy (A., 1904, ii, 262). The appearance of this compound during the reduction coincides with the formation of quinquevalent manganese. The results of the previous paper (*loc. cit.*) have been confirmed from measurements in faintly alkaline solution. In strongly alkaline solution, the reduction of manganate occurs in two phases, which is explained by the formation of mangani-manganate as an intermediate stage. The first phase of the reduction, namely, the formation of mangani-manganate, is accelerated by hydroxyl-ions, whilst the second phase, namely, the reduction of the mangani-manganate, is retarded by hydroxyl-ions.

J. F. S.

The Corrosion of Iron in Water and in Neutral Salt Solutions. JOHN ALBERT NEWTON FRIEND (T., 1923, **123**, 2996—2999).

Ferric Oxide Sols Prepared from Iron Carbonyl. H. FREUNDLICH and S. WOSNESSENSKY (*Kolloid Z.*, 1923, **33**, 222—227).—A clear reddish-brown ferric oxide sol, which is very stable, can be prepared by the oxidation of iron pentacarbonyl. This is effected by shaking the pentacarbonyl with very dilute solutions of hydrogen peroxide. Since in the oxidation the only other products are carbon dioxide, carbon monoxide, and oxygen, the only electrolyte present is carbonic acid, and if this is removed or if the sol is boiled the sol coagulates readily. The coagulum obtained in this way can be readily peptised to form a positive sol by leading a stream of carbon dioxide through it, or by the addition of hydrochloric, nitric, or picric acid, aluminium chloride or ferric chloride. The positive sol can be converted into a negative sol by the addition of sodium hydroxide. The coagulum produced by the addition of electrolytes cannot be again peptised by carbon dioxide. The sol obtained directly from the pentacarbonyl gives the usual precipitation values of a positive sol, but these are considerably smaller than the values obtained with ferric oxide sols prepared by more usual methods. The latter are therefore more stable, and consequently, the sols obtained by peptising the coagulum from the pentacarbonyl sols with ferric chloride are much more stable than sols containing no ferric chloride. A similar result was obtained with sols obtained by using aluminium chloride as peptising agent, but in this case the sols were not so stable as the ferric chloride sols. The lack of stability was much more marked in the case of sols prepared by the use of lanthanum nitrate as peptising agent. The sol from iron pentacarbonyl can be sensitised by the addition of small quantities of albumin, but larger quantities of albumin peptise the ferric oxide coagulum to form a negative sol.

J. F. S.

The Oxidation of Iron Sulphate Solutions in Air. PRAMOD KISER BANERJEE (*Z. anorg. Chem.*, 1923, **128**, 343—349).—Oxidation of ferrous sulphate solutions exposed to air proceeds extremely slowly; by analysis of samples withdrawn at intervals over a period of sixty-two days, it was found that the order of the reaction approaches more nearly that of a unimolecular than that of a bimolecular reaction. Potassium sulphate exerts an accelerating effect, but the sulphates of all other metals tried, and sulphuric acid itself, exert retarding effects, the maximum retarding effect being that of copper sulphate. At higher temperatures, the reaction appears to be very nearly unimolecular. S. I. L.

Precipitation Reactions of Nickel and Cobalt Sulphate Solutions with Zinc or Cadmium at 100°. ROBERT KREMANN, FRANZ ANGELBERGER, FRANZ BAKALARZ, RUDOLF RÖHRICH, and CAMILLO STÖGER (*Z. anorg. Chem.*, 1923, **127**, 316—342).—Zinc or cadmium in the form of turnings or small cylinders was added to solutions containing about 1·4 mol./litre of nickel sulphate or about 0·09 mol./litre of cobalt sulphate. At room temperature, the precipitate contained both metals together with much hydroxide. At 100°, hydroxide is still produced, but in less quantity. It was found that the amount of hydroxide produced increases with the ratio precipitating metal/precipitated metal. It was also found that the surface of the precipitating metal influenced the composition of the precipitate in that as the surface of the precipitating metal increased the percentage of precipitated metal in the precipitate also increased. Measurements were also made of the *E.M.F.* of the precipitated metal/solution against a normal electrode. H. H.

β-Cobalt Iodide. ERWIN BIRK and WILHELM BILTZ (*Z. anorg. Chem.*, 1923, **128**, 45—48).—When ordinary anhydrous cobalt iodide is heated in an evacuated glass tube at 570—575°, at which temperature it boils, part of it sublimes, forming black crystals of the iodide, part decomposes, and a small quantity is deposited high up the tube as a yellow powder. The yellow powder is a second form of cobalt iodide, termed β-cobalt iodide. It is extremely hygroscopic, and dissolves in water to give a bright yellow solution from which chloroform removes free iodine, leaving a colourless solution. This solution will remain colourless for some time, but when warmed or concentrated it acquires the rose colour of an ordinary cobalt iodide solution. Attempts to prepare distinctive hydrates or ammoniates of the β-salt were not successful. E. H. R.

The Binary System Tungsten-Molybdenum. W. GEISS and J. A. M. VAN LIEMPT (*Z. anorg. Chem.*, 1923, **128**, 355—360).—The pure metals in powder form were compressed together in various proportions, and heated to sintering, the melting points of the alloys so obtained being determined by passing currents through filaments of standard cross-section. The melting points all lie on the straight line connecting the melting points of the

pure elements, and the alloys all appear to have homogeneous structures, thus showing that a continuous series of mixed crystals is formed. This conclusion was confirmed by determinations of the temperature coefficients ($\alpha_{20}^{100°}$) of the electrical conductivities, and is in agreement with the remarkable similarity existing between the elements in all respects.

The temperature coefficient may be used to estimate molybdenum in an otherwise pure tungsten; 1% by weight of the former reduces the coefficient by about 10%. S. I. L.

The Precipitation of Tungstic Acid [Tungsten Trioxide]. J. A. M. van Liempt (*Z. anorg. Chem.*, 1923, **127**, 215—220; cf. A., 1922, ii, 773).—The influence of temperature and concentration of acid on the precipitation of tungsten trioxide was studied. The precipitate consists of a mixture of the white and the yellow forms of the trioxide, together with an adsorption compound with water. Temperature has little effect on the precipitation, but in order to obtain the precipitate in a granular and easily manipulated form, it is advisable to use hydrochloric or nitric acid in high concentration, and in excess. H. H.

The Ammines of Bivalent Tin. Wilhelm Biltz and Wilhelm Fischer (*Z. anorg. Chem.*, 1923, **129**, 1—14).—The following compounds were investigated, the temperature at which the dissociation pressure equals 100 mm. and the heats of dissociation per molecule of ammonia having been determined. $SnCl_2,9NH_3$, −55°, 7·6 Cal.; $SnCl_2,4NH_3$, −15°, 9·3 Cal.; $SnBr_2,9NH_3$, −57°, 7·55 Cal.; $SnBr_2,5NH_3$, −2°, 9·8 Cal.; $SnBr_2,3NH_3$, 66°, 12·5 Cal.; $SnBr_2,2NH_3$, −102°, 13·6 Cal.; $SnI_2,10NH_3$ or $9NH_3$, −48°, 7·9 Cal.; $SnI_2,5NH_3$, 10°, 10·2 Cal.; $SnI_2,3NH_3$, 55°, 11·9 Cal.; $SnI_2,2NH_3$, 94°, 13·3 Cal.; SnI_2,NH_3, 157°, 16 Cal. Heats of solution in 1% hydrochloric acid of $SnCl_2$ +0·8 Cal., $SnBr_2$ −1·6 Cal., SnI_2 −5·8 Cal. Heats of formation were measured tensimetrically and calorimetrically and the results agreed well. Decrease in the stability of the complexes in passing from the chloride to the bromide and to the iodide was not observed. For the compounds with the higher co-ordination numbers, the authors suggest the formation of two shells of ammonia around the central atom, and in the case of stannous bromide the co-ordination numbers are assumed to be 3+2 and 3+6. The preparation of all the compounds is described. All except $SnCl_2,4NH_3$ and $SnI_2,2NH_3$ are new compounds. W. T.

The Binary Halides of the Quadrivalent Elements. I. Quadrivalent Tin. Mathias G. Räder (*Z. anorg. Chem.*, 1923, **130**, 325—332).—Examination of the melting-point curves of mixtures of pure stannic bromide and iodide, and analysis of the crystals first separated on cooling, show that no mixed halogen compounds as described in the literature really exist. The method given by Lenormand (A., 1899, ii, 33, 745) for the preparation of $SnBr_2I_2$ by heating stannous bromide with excess of iodine in sealed tubes at 100° is found in fact to yield an equimolecular mixture of stannic bromide and stannic iodide. S. I. L.

The Reduction of Inorganic Halides. II. The Reduction of Titanium Tetrachloride. OTTO RUFF and FRANZ NEUMANN (*Z. anorg. Chem.*, 1923, **128**, 81—95).—The reduction of titanium tetrachloride with different elements was studied. Sodium amalgam reduces it slowly to dichloride in the cold, but if the action is too prolonged, trichloride is formed by interaction of the dichloride with tetrachloride. Magnesium, zinc, aluminium, arsenic, and antimony reduce the tetrachloride to trichloride, the reaction being accelerated by a small quantity of anhydrous aluminium chloride; phosphorus and sulphur reduce the tetrachloride only in presence of aluminium chloride. Reduction of titanium tetrachloride with aluminium powder in presence of aluminium chloride affords a new and effective method for preparing titanium trichloride. The reaction is carried out in a closed, evacuated tube at 200—250°. The trichloride obtained, freed from tetrachloride and from aluminium chloride by distillation, is in a finely divided, non-crystalline form, of a bright violet colour. It is very sensitive to oxygen and moist air. When heated with sulphur, it forms titanium chlorosulphides of varying composition, $Ti_5Cl_4S_{12}$ to $Ti_4Cl_2S_{12}$, and it also forms similar compounds with selenium. When titanium trichloride is heated at 425° at less than 1 mm. pressure, it volatilises practically unchanged and the trichloride crystallises on the colder parts of the tube in dark violet prisms. At 450° and above, the trichloride decomposes (at <1 mm. pressure) into tetrachloride and dichloride. The dichloride remains as a black powder when the trichloride is heated at 475° and the tetrachloride vapour is pumped away as it is formed. Titanium dichloride is extraordinarily reactive, takes fire in moist air, and decomposes water at once with evolution of hydrogen. It is not volatile at 600° at very low pressures.

E. H. R.

Reduction of Inorganic Halides. III. The Reduction of Zirconium Tetrachloride. OTTO RUFF and RICHARD WALLSTEIN (*Z. anorg. Chem.*, 1923, **128**, 96—116).—Zirconium tetrachloride can be reduced by a number of metals and metalloids, including aluminium, magnesium, zinc, arsenic, antimony, lead, tin, mercury, bismuth, and phosphorus, to a greater or less extent, at temperatures above 250° in presence of aluminium chloride, in absence of air. The most suitable reducing agent is aluminium powder in presence of aluminium chloride at 300°. At this temperature, zirconium tetrachloride does not react with alumina, but zirconia reacts completely with aluminium chloride according to the equation: $3ZrO_2+4Al_2Cl_3 \longrightarrow 3ZrCl_4+2Al_2O_3$. When zirconium tetrachloride is heated in a vacuum at this temperature with the theoretical quantity of aluminium for the reaction $3ZrCl_4+Al=3ZrCl_3+AlCl_3$, and the aluminium chloride and unchanged zirconium tetrachloride are removed by sublimation, a residue is left consisting largely of *zirconium trichloride*, which, however, cannot be obtained in a pure condition. The trichloride is a brown, microcrystalline solid, d^{18} 3·0. It is rapidly oxidised by air to

oxychloride and decomposes water with evolution of hydrogen and formation of $ZrOCl_2$. Concentrated hydrochloric acid retards the reaction with water, and a brown solution of zirconium trichloride is obtained which slowly loses its colour as oxidation proceeds. When heated in absence of air at about 330°, the trichloride decomposes into a mixture of di- and tetra-chloride: $2ZrCl_3=ZrCl_2+ZrCl_4$, and when the tetrachloride is removed as fast as it is formed by a vacuum pump, the *dichloride* remains as a black, amorphous substance, d^{18} 3·6. It is practically insoluble in air-free water, and is only slowly decomposed by moist air or water. It is oxidised by concentrated acids with evolution of hydrogen and formation of the quadrivalent zirconium salt. Above 600°, it decomposes into zirconium tetrachloride and zirconium.

E. H. R.

Crystal Structures of Vanadium, Germanium, and Graphite. ALBERT W. HULL (*Physical Rev.*, 1922, **20**, 113).—The powder method of examination shows that vanadium has a body-centred cubic lattice of side 3·04 Å., distance between nearest atoms 2·63 Å., ideal density 5·96. Germanium has the same crystal structure as diamond; corresponding values are 5·63 Å., 1·218 Å., and 5·36. It is confirmed that the lattice of graphite is of the hexagonal close-packed type, and not rhombohedral as found by Debye.

A. A. E.

Dispersoid Synthesis of Gold. I. P. P. VON WEIMARN (*Kolloid Z.*, 1923, **33**, 228—247).—A general preliminary communication in which after a discussion of dispersoid synthesis, an account is given of experiments on the dispersoid synthesis of gold by the formaldehyde method, the phosphorus method, the citrate or tartrate method, and the glycerol method. In the general discussion, the author examines the conditions which control the size of the colloidal particles, and the reversibility and the stability of sols. The influence of impurities and added foreign substances is also discussed. The stability, size of particles, colour, and other characteristics of gold sols prepared under various conditions by the above-named methods are discussed. J. F. S.

Mineralogical Chemistry.

Presence of Anhydrous Sodium Sulphate among the Products of the Present Activity of Vesuvius. FERRUCCIO ZAMBONINI (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 122—124).—The products of the present activity of Vesuvius include anhydrous sodium sulphate in the form of thénardite. T. H. P.

The Existence of Brochantite in Katanga. ALFRED SCHOEP and GEORGES BUYSSE (*Bull. Soc. Belge Géol.*, 1923, **33**, 72—73; *Bull. Soc. Chim. Belg.*, 1923, **32**, 342—343).—Minute, greenish-

blue needles on quartz crystals in a sample of copper ore have the optical constants of brochantite and gave:

CuO.	SO_3.	H_2O.	sp. gr.
69·11	17·07	13·81	3·88

L. J. S.

The Presence of Carnotite in the Congo. ALFRED SCHOEP and ÉMILE RICHET (*Bull. Soc. Belge Géol.*, 1923, **32** [for 1922], 150—152; *Bull. Soc. Chim. Belg.*, 1923, **32**, 340—341).—A yellow, crystalline powder in red sandstone from Katanga is proved to be carnotite. The minute crystals are rhombic scales with an angle of 77—78·5°; the optic axial plane is parallel to the shorter diagonal and the acute negative bisectrix normal to the plate. The material dissolves in hydrochloric acid to a blood-red solution, this colour (due to vanadium) being lost on heating. L. J. S.

A Black Mineral Associated with Carnotite from the Congo. ALFRED SCHOEP (*Bull. Soc. Belge Géol.*, 1923, **33**, 85—86; *Bull. Soc. Chim. Belg.*, 1923, **32**, 344—345).—A red, calcareous sandstone containing carnotite (preceding abstract) shows black lenticles and irregular stains. The lenticles dissolve in strong hydrochloric acid with evolution of chlorine yielding a green solution. Analysis gave:

SiO_2.	CoO.	Fe_2O_3.	Mn_3O_4.
44·15	2·18	4·70	3·60

The remainder being water and calcium and magnesium carbonates. The black colloidal material is compared with heubachite, transvaalite, etc. L. J. S.

Chinkolobwite. A New Uranium Mineral from Katanga. ALFRED SCHOEP (*Bull. Soc. Belge Géol.*, 1923, **33**, 87—88; *Bull. Soc. Chim. Belg.*, 1923, **32**, 345—346).—A specimen of massive soddite (A., 1922, ii, 451) from Chinkolobwe, is partly covered with a felt of fine needles of a canary-yellow colour. These at first sight resemble the prismatic type of soddite, but they show a lower birefringence and other differences in their optical characters. Microchemical tests show the presence of uranium and silica, and the mineral is perhaps dimorphous with soddite, $12UO_3,5SiO_2,14H_2O$. L. J. S.

Analytical Chemistry.

A New Absorption Pipette for Gas Analysis. SIDNEY WALTER SAUNDERS (T., 1923, **123**, 2826—2828).

Volumetric Analysis. M. EMM. POZZI-ESCOT (*Ann. Chim. Analyt.*, 1923, [ii], **5**, 293).—Fabaron has recently (*ibid.*, 161) suggested the use of graduated tubes for measuring the volumes of precipitates, but the author points out that he had described this method previously (A., 1908, ii, 539). W. P. S.

Replacement of Iodine by Ferric Chloride in Volumetric Analysis. KARL JELLINEK and LEO WINOGRADOFF (*Z. anorg. Chem.*, 1923, **129**, 15—32).—This new method is based on the reaction $2FeCl_3+Na_2S_2O_3=2FeCl_3+2NaCl+Na_2S_4O_6$, and can be employed for the estimation of oxidising and reducing agents. The titrations must be carried out with hot solutions and in an atmosphere of carbon dioxide. The solutions recommended are 0·1*N*-ferric chloride+0·2% hydrochloric acid and 0·1*N*-sodium thiosulphate+0·1% sodium carbonate. The ferric solution is kept at 50—60° and the thiosulphate solution run in from a burette; this causes the formation of a violet coloration probably due to the formation of the unstable ferric thiosulphate, which rapidly disappears; the end-point is reached when no further coloration is produced; the presence of more than 0·5% hydrochloric acid makes the colour very indistinct. Thiocyanate or potassium iodide starch paper cannot be employed as indicators for the complete reduction of ferric-ion in this case, but the disappearance of the characteristic colours with phenols gave good results, *e.g.*, 1 c.c. saturated solution of salicylic acid. The end-point was also sharply given by the decoloration of methylene-blue, this being due to the presence of thiosulphuric acid; still better results were obtained by using a mixture of methylene-blue and magenta (5 drops of a 0·5 % solution of aqueous methylene-blue and 3 drops of saturated aqueous magenta). Attempts to use as the end-point the decoloration of organic dyes by the sulphur dioxide formed did not give satisfactory results. Details are given of the estimation of potassium permanganate, potassium chlorate, manganese dioxide, tin (in white metal), and sulphides. Unsatisfactory results were obtained in the estimation of nitrates, hydrogen peroxide, and sulphites. W. T.

New Methods in Alkalimetry and Acidimetry, and in Oxidimetry. Hydrolytic Precipitation Analysis and Mercurimetry. K. JELLINEK and P. KREBS (*Z. anorg. Chem.*, 1923, **130**, 263—324).—In place of the usual organic colour indicators, the following inorganic salts may be used in titrations of acids and alkalis: (*a*) Lead salts for all alkalis, and for acids other than sulphuric; (*b*) copper salts for all acids with ammonia; (*c*) silver salts for all acids other than the halogen acids, and for all alkalis other than ammonia, and (*d*) ferric thiocyanate for all strong acids and alkalis. With (*a*), (*b*), and (*c*) the quantity of indicator used must be as small as possible; excess of alkali is added to the acid solution containing the indicator, and the excess titrated back until the cloudiness due to precipitation of the heavy metal hydroxide disappears. The average results with (*a*) are 0·6% too high in determining the alkali, with (*b*) 0·6% too high, and with (*c*) 2·5% too high; these average errors must be taken into account for very accurate estimations. Using (*d*), the average error is only 0·1%; the indicator is used in the form of 1 drop of a 0·25% ferric chloride solution and 10 drops of a 10% potassium thiocyanate solution.

A suitable method for the titration of ferrous and stannous salts consists in oxidation with hydrogen peroxide solution, using as indicator a titanic salt in presence of sulphuric acid. To reduce the coloration due to the ferric salt formed, orthophosphoric acid is added, the error being 0·5%; with tin salts, the average error is negligible. Ferrous salts are titrated in the cold, tin salts at a high temperature. The method is unsuitable for arsenic and antimony salts, and for oxalates.

A titration method for the estimation of cadmium and nickel consists in precipitating as hydroxide by means of excess of standard alkali at the boiling point. After cooling, a few drops of silver nitrate are added, and the liquid is titrated with standard acid until the yellow coloration disappears. A comparison solution is required in each case, and a separate determination of the amount of alkali required to make the original solution neutral must also be made. For cadmium, the results are very accurate; for nickel, the average error is +0·3%, probably due to oxidation.

The hydrolytic precipitation method described by Jellinek and Czerwinski (this vol., ii, 878) has been further examined for the estimation of (1) lead by means of potassium chromate, and extended to (2) disodium hydrogen arsenite, (3) disodium sulphide, (4) sodium carbonate, and (5) potassium cyanide as precipitation reagents. The solutions to be titrated must be exactly neutralised in each case. Method (2) was found unsuitable for zinc, but suitable for lead and cadmium, the discrepancies being within the limits of experimental error. Phenolphthalein is employed as indicator, and comparison solutions without indicator must be used. Precipitation is effected at the boiling point, and the arsenite solution must be standardised each time against the pure metal salt solution. With (3), very accurate results are obtained for zinc salts, and the analysis may be applied to the estimation of zinc in white metals and other alloys. The indicator used is methyl-red, and the sodium sulphide solution must be standardised by means of pure zinc at fortnightly intervals. The method is rapid and convenient. Both zinc and lead may also be estimated accurately with (4), using phenolphthalein as indicator; the neutralised solution is boiled with excess of the carbonate solution, the excess being titrated back at 100° with a standard zinc or lead solution, respectively, until the red coloration disappears. Comparison solutions must be employed. Neither of these metals can be accurately estimated by means of (5), but with silver excellent results are obtained; phenolphthalein is used as indicator, and precipitation carried out at the boiling point.

Mercuric salts may also be estimated by means of (5), the cyanide solution being added at the boiling point until the indicator, phenolphthalein, becomes rose-coloured. A constant error of 3·1% (low) is observed, but if the cyanide be standardised by means of a mercuric salt, this error automatically disappears. By reason of the slight dissociation of mercuric salts, these promise to be of great value in connexion with this method of analysis.

S. I. L.

Use of Calcium Carbonate in Volumetric Analysis. E. Kordes (*Z. anal. Chem.*, 1923, **63**, 117—120).—For the estimation of free chlorine in solutions which cannot be titrated directly, the chlorine may be expelled by generating carbon dioxide in the solution by the action of hydrochloric acid on thick pieces of calcium carbonate (marble) and collecting the evolved gases in potassium iodide. In estimating the available oxygen in manganese dioxide, for instance, a weighed quantity of the substance is introduced into a conical flask together with two thick pieces of marble and hydrochloric acid is dropped on to the dioxide by means of a dropping funnel. When the latter has dissolved, after gentle heating, if necessary, the flask is inclined so that the marble comes into contact with the liquid. The carbon dioxide evolved sweeps the chlorine formed in the first stage into receiving flasks containing potassium iodide and the liberated iodine is titrated as usual. The whole process takes ten minutes against the forty-five minutes consumed if carbon dioxide is passed through the apparatus in the usual way. A. R. P.

Use of the Mercury Electrode for Electrometric Titration of Halides, Cyanides, Sulphides, and Thiosulphates. I. M. Kolthoff and E. J. A. H. Verzyl (*Rec. trav. chim.*, 1923, **42**, 1055—1064).—Methods are described for the potentiometric estimation of chlorides, bromides, iodides, cyanides, sulphides, and thiosulphates. The alteration of the *E.M.F.* of the solution (Δa) in contact with a mercury electrode with a small change in concentration of mercuric chloride (Δc) is measured, and the end-point is indicated when $\Delta a/\Delta c$ reaches its maximum value. Chlorides and bromides can be determined, but not together in the same solution. Iodides can be estimated even in great dilution, but large quantities of bromides interfere. Cyanides and thiocyanates can be estimated. Sulphides may be estimated in great dilution, especially in alkaline solution, but strong solutions are best titrated with silver nitrate. Salts with bivalent anions depress the results slightly. Thiosulphates and sulphides may be estimated in mixtures of the two, provided neutral solutions are employed. H. H.

Estimation of Sulphur in Cast Iron. Sansei Kitajima (*Rikwagaku Kenkyujo Ihô*, 1923, **2**, 243—258).—The author has examined the usual method of estimating sulphur in iron, by dissolving in hydrochloric acid and determining the amount of hydrogen sulphide evolved, and finds that the rate at which the hydrochloric acid is added to the sample has a considerable effect on the result. Hydrochloric acid (d 1·19—1·20) diluted with twice its volume of water is to be used for the operation and 10 c.c. of cadmium chloride solution (prepared from 120 grams of cadmium chloride, 1,500 c.c. of water, and 600 c.c. of ammonia, d 0·90) diluted with 35 c.c. of water. The volume of the solution for the titration should be about 70 c.c. for 5 grams of the sample. If the evolved hydrogen sulphide is passed through a quartz tube heated to redness before entering the cadmium chloride solution, the result is slightly higher and more constant; in this case the results obtained

by the titration and by weighing as barium sulphate after oxidising the cadmium sulphide with bromine water are almost identical. The solution and residue remaining in the flask after the evolution has ceased are almost free from sulphur. K. K.

Estimation of Sulphate at Great Dilutions by Hahn's Method. I. M. KOLTHOFF and M. J. VAN CITTERT (*Pharm. Weekblad*, 1923, **60**, 1177—1190).—A critical examination has been made of Hahn's method (this vol., ii, 39, 339). The present authors filter the barium sulphate through a wad of cotton, as suggested by Winkler (*Z. angew. Chem.*, 1917, **30**, 251), and carry out the final washing with alcohol. The method gives results 1·0—1·3% too low, but by working in acetic acid or neutral solution instead of in hydrochloric acid solution a high degree of accuracy is obtained. Barium chloride gives better results than barium nitrate.

The alkali metals and aluminium and ferric salts do not affect the results, but calcium interferes unless the precipitation is carried out in *N*/10-hydrochloric acid solution. Nitrates have little influence, but the presence of phosphates make the results too high. If the operation is carried out at atmospheric temperature, the errors are much higher; this is also the case if the reagents are heated in a sealed tube above 260°. S. I. L.

Limitations of the Reaction between Ammonia and Sodium Hypobromite. DINSHAW RATTONJI NANJI and WILLIAM SIMPSON SHAW (*Analyst*, 1923, **48**, 473—477).—Critical examination of the hypobromite method showed that it was untrustworthy for the estimation of ammonia, particularly for small quantities of the latter. When dealing with amounts of ammonia varying from 3 to 17 mg., the results obtained were from 2 to 7% too high. Traces of nitrates and nitrites were always formed as by-products of the reaction. W. P. S.

Cause of Error in the Jodlbauer Method of Estimating Total Nitrogen. JEAN BORDAS (*Compt. rend.*, 1923, **177**, 696—697).—The Jodlbauer method gives a low result with complex fertilisers, etc., containing tannins. These, as well as pyrogallol, quinol, and pyrocatechol (but not resorcinol or non-reducing diphenols) effect partial reduction of nitrate in presence of concentrated sulphuric acid, perceptible evolution of nitrous fumes occurring. The methods of Dumas, of Salle, or of Devarda (followed by a Kjeldahl determination of nitrogen not present as nitrate) are to be preferred in these cases. E. E. T.

The Determination of Protein Nitrogen according to Stutzer. S. KOSTYTSCHEV (*Z. physiol. Chem.*, 1923, **130**, 34—38).—Stutzer's method for determining protein nitrogen, in which the proteins are precipitated by heating with copper hydroxide, is inaccurate. Nitrogen other than protein nitrogen is precipitated by the reagent. W. O. K.

Analysis of Monosodium Phosphate and Phosphoric Acid. FRANK X. MOERK and EDWARD J. HUGHES (*Amer. J. Pharm.*, 1923, **95**, 671—678).—The following volumetric method is described: 40 c.c. of $N/10$-silver nitrate solution and 0·2 c.c. of methyl-red solution are treated with dilute sodium hydroxide solution until the red coloration changes to yellow; 10 c.c. of the phosphate solution (containing about 0·2 g. of the salt) are then added, and the mixture is titrated with $N/10$-sodium hydroxide solution. The reaction proceeds according to the equation $NaH_2PO_4+3AgNO_3+2NaOH=Ag_3PO_4+3NaNO_3+2H_2O$. One hundred c.c. of 10% sodium chloride solution and 0·2 c.c. of phenolphthalein solution are treated with sodium hydroxide solution until a distinct red coloration is obtained; the solution is divided into two equal parts, to one is added 10 c.c. of the phosphate solution and the mixture is titrated with $N/10$-sodium hydroxide solution until the coloration is equal to that of the reserved portion. The equation for this titration is $NaH_2PO_4+NaOH=Na_2HPO_4+H_2O$. If the two titrations yield the same percentage of monosodium phosphate, the sample is free from disodium phosphate and phosphoric acid; a higher percentage by the phenolphthalein method indicates the presence of free phosphoric acid, whilst a higher percentage by the methyl-red method denotes the presence of disodium phosphate in the sample. The quantities of free phosphoric acid and disodium phosphate may be calculated from the results obtained. The sodium chloride solution used must not contain calcium salts and the sodium hydroxide solution must be free from carbonate. The method may be applied to phosphoric acid. W. P. S.

Chemistry of the Reinsch Test for Arsenic and Antimony, and its Extension to Bismuth. B. S. EVANS (*Analyst*, 1923, **48**, 417—429).—The results obtained in an investigation of the Reinsch test favour the hypothesis that the reaction is due to reduction of the arsenic, antimony, or bismuth salt by a film of hydrogen on the surface of the copper, the hydrides formed in the first two instances combining with the copper to form arsenide or antimonide, respectively. When oxidation of the cuprous chloride formed is prevented by carrying out the test in an atmosphere of carbon dioxide, the deposition of the three elements is complete; in the case of relatively large amounts of antimony, the deposit may be so dense that the reaction ceases, and the solution may need to be treated with two or three successive pieces of copper foil. With small quantities (1 to 5 mg.) of bismuth better results are obtained by using acetic acid and sodium chloride in place of sulphuric acid and sodium chloride. W. P. S.

Estimation of Arsenic in Arsenobenzenes. F. DE MYTTENAERE [with VAN BOECKEL, MUSET, and DUMONT] (*Chim. et Ind.*, 1923, **10**, 403—410).—About 0·2 g. of the arseno-compound is dissolved in 5 c.c. of water, 10 c.c. of hydrogen peroxide (10 vols.), and 10 c.c. of 50% sulphuric acid are added and the mixture is boiled until the excess of peroxide is decomposed; a further 5 c.c. of hydrogen peroxide are then added, and the heating is continued

until sulphuric acid fumes are evolved. After cooling, the mixture is diluted with 10 c.c. of water, a slight excess of 1% potassium permanganate solution is added, and the pink coloration is discharged by the addition of a drop of oxalic acid solution; 20 c.c. of 25% potassium iodide solution are added, the mixture is heated on a water-bath for twenty minutes, cooled, and decolorised exactly by the addition of $N/10$-sodium thiosulphate solution. Twenty-five c.c. of saturated sodium carbonate solution and an excess of sodium hydrogen carbonate are then added, and the solution is titrated with $N/10$-iodine solution. Each c.c. of the latter solution is equivalent to 0·003749 g. of arsenic. The quantity of arsenic present should be from 19 to 21%, and the ratio arsenic/nitrogen should not be less than 5·6. W. P. S.

A New Gas Combustion Furnace. THOMAS J. HEDLEY (*J. Soc. Chem. Ind.*, 1923, **42**, 432—433T).—A somewhat fuller description of the furnace previously described (T., 1921, **119**, 1242). E. H. R.

Estimation of Carbon Monoxide in Air. VIKTOR ANDRISKA (*Z. Unters. Nahr. Genussm.*, 1923, **46**, 43—46).—Weltzl's tannin reaction with defibrinated blood solution in which carbon monoxide has been absorbed from the air is developed into a quantitative method of determining carbon monoxide in air. The sensitiveness of the test was found to be 1% of the volume of blood solution (1 part of blood to 4 parts of water) employed, so that 100 c.c. of blood solution will detect 1 c.c. of carbon monoxide. Absorption vessels are not suitable for estimating small proportions of carbon monoxide in air, as losses occur. A more complete absorption is obtained by shaking up the blood solution with one hundred times its volume of air in a closed vessel. A hollow stopper capable of containing 50 c.c. of blood solution, which can be fitted to a 5-litre flask, is illustrated. This is so designed that the blood solution is projected into the flask in a thin stream, so as to effect a complete absorption of the carbon monoxide. After absorption is complete (3 hours), known volumes of the blood solution are diluted with known volumes of the fresh blood solution, the total volume of the mixture being in each case 5 c.c. Fifteen c.c. of a freshly prepared 1% tannin solution are added to each mixture and that mixture noted, the colour of which can just be differentiated from the blank test with fresh blood solution only, after remaining for twenty-four hours. In this way, accurate estimations of carbon monoxide in air are possible down to 0·02%. H. C. R.

A Microchemical Method for the Analysis of Carbonates. MIECZYSŁAW DOMINIKIEWICZ (*Roczniki Chemji*, 1923, **3**, 165—176).—Naturally occurring carbonates can be divided into two groups according to their behaviour on heating on platinum foil below red heat; the first group includes those which are not visibly changed by this treatment (calcite, aragonite, lublinite, dolomite, magnesite, witherite, strontianite, baryocalcite, etc.) and those which change colour under the same conditions (siderite, rhodochrosite, oligonite, ankerite, brennerite, cernosite, plumbocalcite, smith-

sonite, and calcites and dolomites containing iron or manganese); naturally coloured minerals such as malachite are not taken into consideration.

Of the minerals of the first groups only two—strontianite and witherite—are completely unaffected by heating; the remainder suffer some degree of dissociation with the formation of oxides which can be detected by suitable reagents. The grains of mineral are treated, after heating, with an alcoholic solution of alizarin (0·1%); those which contain an oxide are coloured bluish-red, whilst strontianite and witherite remain colourless. Dianil-green in aqueous solution can also be used for the same purpose, but the use of 1% alcoholic phenolphthalein is preferable because it allows a further distinction to be made between the minerals of this group. The coloured phenolphthalein salt formed with magnesium is insoluble in alcohol and only slowly dissolves in water, whilst the calcium salt is readily soluble. Magnesite is thus readily recognised because the grains of mineral become coloured, but the solution remains colourless; the solution slowly becomes pink in the case of dolomite, whilst an immediate coloration is obtained with calcite, etc. Dolomite can, moreover, be distinguished from magnesite, because the latter, when heated and then warmed for ten minutes with 5% aqueous sodium hydroxide followed by a 0·1% aqueous solution of the ammonium salt of 2 : 4 : 6 : 7-tetrahydroxyfluoran (Liebermann, A., 1901, i, 595), is coloured crimson, whilst dolomite remains colourless. Predacite, when heated on platinum foil for a few seconds below red heat and then treated with phenolphthalein, is coloured in places only, and the alcoholic solution remains colourless, as the mineral is composed of a mixture of calcite and brucite, the former of which is not decomposed by this treatment; staining with tetrahydroxyfluoran after treatment with alkali produces a similar effect. Calcite can be distinguished from aragonite by heating the mineral for two minutes with 0·25% aqueous cobalt nitrate (compare Meigen, A., 1901, ii, 692), washing, and staining with tetrahydroxyfluoran. On heating with dilute ammonia, aragonite remains crimson, whilst calcite is decolorised. Ferrous sulphate (1%) can replace cobalt nitrate in this test, the dye being used in alkaline solution; aragonite is coloured blue, but calcite remains colourless. Calcite, aragonite, witherite, and strontianite are coloured violet when treated after heating with 0·3% ferric chloride for twelve seconds, followed by a neutral solution of the dye and finally ammonia; dolomite is unaffected.

In order to distinguish witherite from strontianite, the mineral is warmed for one to two minutes with 0·5% chromic acid, when witherite is coloured yellow; the colour can be intensified by subsequent treatment with a lake-forming dye such as chromotrope-2*B*.

Of the minerals of the second group, siderite and rhodochrosite become black and lustrous on heating, and the former is also magnetic; calcites and dolomites containing iron or manganese become light brown to black; smithsonite shows a yellow coloration while hot, and becomes colourless or black on cooling, whilst cerussite is coloured light-brown and does not change on cooling.

They can also be distinguished by warming with 5% aqueous sodium hydroxide for fifteen to twenty minutes and with tetrahydroxyfluoran for five to ten minutes. The colours produced are: siderite, purplish-brown; rhodochrosite, brownish-crimson; smithsonite, orange. A further test consists in heating for ten to fifteen minutes with 5% sodium hydroxide and a drop of bromine, then with sodium hydroxide alone, and finally with a saturated solution of benzidine in acetic acid; minerals containing manganese are coloured an intense blue (*e.g.*, rhodochrosite).

In a few cases it was found that iron present in some dolomites and calcites was not detected by the tetrahydroxyfluoran test; it is suggested that the iron was present in the form of a definite double carbonate, similar to the calcium magnesium carbonate which constitutes dolomite.

Smithsonite can be recognised by Lemberg's method (*Z. deutsch. Geolog. Ges.*, 1887, 357) in addition to the above, and this also applies to cerussite. The latter and also plumbocalcite can, however, be recognised by the benzidine test described above; an intense blue coloration, changing to violet, is observed in these cases.

G. A. R. K.

Sodium 6-Chloro-5-nitro-*m*-toluenesulphonate—a New Reagent for Potassium. HERBERT DAVIES and WILLIAM DAVIES (T., 1923, **123**, 2976—2982).

Quantitative Analysis by Hydrolytic Precipitation. K. JELLINEK and J. CZERWINSKI (*Z. anorg. Chem.*, 1923, **30**, 253—262).—If to a slightly acid solution of barium chloride coloured red by addition of methyl-orange, excess of potassium chromate solution is added, the colour changes from red to yellow; as soon as the equivalent quantity of potassium chromate has been added, any excess is hydrolysed and the solution acquires an alkaline reaction. Consideration of the degrees of dissociation and of the hydrogen-ion concentrations of the common indicators shows that high degrees of accuracy may be expected by applying the principle to any case in which soluble combinations of weak acid with strong base or strong acid with weak base may be utilised. Thus barium chloride may be estimated by means of potassium chromate, using methyl-red, with an error of 0·06%; by adding a known excess of barium chloride, sulphates may be similarly estimated. Cadmium salts do not interfere. Similarly, lead nitrate may be estimated by means of potassium chromate, using methyl-red. The titrations are carried out in porcelain dishes. The new method allows of rapid and accurate titrations in many cases in which gravimetric analysis is tedious and difficult. S. I. L.

The Separation of Magnesium from the Alkali Metals by Means of Organic Bases. GUNHILD HEMMING (*Z. anorg. Chem.*, 1923, **130**, 333—342).—A solution of guanidine (prepared by addition of a slightly insufficient amount of barium hydroxide to the carbonate) precipitates magnesia quantitatively in presence of the alkali metals if excess be used; ammonium salts interfere.

The method may be employed in titration, but since guanidine solutions do not keep well, standard solutions of the carbonate and baryta may be employed. Piperidine does not give quite such good results, but the solution may be kept without change. Aliphatic amines are not so suitable, the errors being greater.

S. I. L.

A New Microchemical Reaction for the Estimation of Zinc. G. SPACU and R. RIPAN (*Bul. Şoc. Ştiinţe Cluj*, 1922, **1**, 576—580; from *Chem. Zentr.*, 1923, iv, 185; cf. this vol., ii, 699).—The double compound of the composition $[Zn(C_5H_5N)_2](CNS)_2$ formed by the reaction of ammonium thiocyanate and pyridine with a zinc salt is dissolved by repeated extraction with small quantities of chloroform. After evaporation to dryness of the chloroform solution, the residue is weighed. G. W. R.

The Electrometric Titration of Zinc and Cadmium. FRIEDR. MÜLLER (*Z. anorg. Chem.*, 1923, **128**, 125—130).—In confirmation of the results of Hedrich (*Diss. Dresden*, 1919) it is found that zinc can be titrated electrometrically with potassium ferrocyanide, using a platinum indicator-electrode, with an accuracy of 0·2—0·3%; the precipitate is $K_2Zn_3(FeC_6N_6)_2$, and the results are best with hot neutral solutions. Cadmium may be similarly titrated, the precipitate being $K_2Cd(FeC_6N_6)$. With sodium ferrocyanide, cadmium gives accurate results, but with zinc poor results were obtained. No advantage is gained by addition of salts of rubidium, cæsium, or lithium. Zinc in presence of cadmium may be accurately titrated with potassium ferrocyanide, but the cadmium can be estimated in the solution only by the use of an empirical factor.

S. I. L.

Estimation of Zinc and Lead in Presence of Large Amounts of Carbon. W. KAHLBAUM (*Eng. Min. J. Press*, 1923, **116**, 110—111).—The carbonaceous matter is destroyed in 0·5 g. of the material by heating with 5—10 g. of sodium peroxide in a mild steel bomb of Parr's type. The mass after reaction is extracted with water, and the insoluble hydroxides are dissolved in dilute acid. For the estimation of zinc, 5 g. of ammonium chloride, 20 c.c. of ammonia solution, and a little hydrogen peroxide are added, the liquid is filtered, and titrated with potassium ferrocyanide solution. Lead is estimated by the molybdate method or, if present in only a small quantity, electrolytically. CHEMICAL ABSTRACTS.

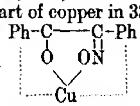
A New Reaction for Cadmium. G. SPACU (*Bul. Şoc. Ştiinţe Cluj*, 1922, **1**, 538—541; from *Chem. Zentr.*, 1923, iv, 187).—By the addition of potassium thiocyanate solution to an aqueous solution of a cadmium salt in the presence of pyridine, a white crystalline precipitate having the composition $[Cd(C_5H_5N)_2](CNS)_2$ is obtained. It is soluble in excess of pyridine and is decomposed by acids. By this reaction, 0·02 g. of cadmium per litre may be detected. G. W. R.

The Estimation of Lead as Cyanide. W. HERZ and EBERHARD NEUKIRCH (*Z. anorg. Chem.*, 1923, **130**, 343—344).—Lead is pre-

cipitated quantitatively in the cold by gradual addition of considerable excess of normal sodium cyanide solution ; the precipitate is collected, dried, and weighed as $Pb(CN)_2$. Neither copper nor silver interferes. S. I. L.

Nature of the Oxide Produced on the Anode during the Electrolysis of Thallous Sulphate. A. GUTBIER and W. DIETERLE (*Z. Elektrochem.*, 1923, **29**, 457—467).—The authors have examined the methods of Heiberg (A., 1903, ii, 614) and of Gallo and Cenni (A., 1908, ii, 986) for the electrolytic estimation of thallium, which consists in the deposition of the oxide on the anode. It is shown that the oxide invariably contains sulphuric acid. Consequently, neither method is trustworthy for the exact estimation of thallium. It is shown that thallium may be estimated by the electro-deposition of oxide as follows: thallous sulphate is dissolved in 100 c.c. of water in a roughened platinum dish, 0·1—1·5 c.c. of $2N$-sulphuric acid and 5—9 c.c. of ethyl alcohol are added, and the solution is electrolysed at 53—58°, when the oxide Tl_2O_3 is deposited quantitatively. It is shown that the anodic product is definitely Tl_2O_3, and not Tl_3O_5, as suggested by Gallo and Cenni (*loc. cit.*). J. F. S.

A New Specific Reagent for the Estimation of Copper. F. FEIGL (*Ber.*, 1923, **56**, [*B*], 2083—2085).—The name " Cupron " is proposed for benzoinoxime, which precipitates copper quantitatively from neutral or ammoniacal solution. The precipitate is sap-green in colour, and is insoluble in water, alcohol, dilute ammonia, acetic acid, or tartaric acid. It is easily soluble in dilute mineral acids, and fairly soluble in concentrated ammonia. The reagent is specific for copper in ammoniacal or tartrate solution, in that iron, lead, cobalt, nickel, zinc, and aluminium are not precipitated. It is sensitive to one part of copper in 33,000 parts, and the annexed co-ordination formula



is proposed for the copper derivative. This contains 22·02% Cu and may be dried in the air oven at 110°. H. H.

Simultaneous Electrometric Estimation of Copper and Silver by Means of Potassium Thiocyanate. ERICH MÜLLER and ARTHUR RUDOLPH (*Z. anal. Chem.*, 1923, **63**, 102—111).—Copper may be determined electrometrically by measuring the change of potential between a copper indicator electrode and the usual normal calomel electrode at 70° in a solution containing sodium hydrogen sulphite to which standard potassium thiocyanate is slowly added. The solution must contain more copper than corresponds with a $M/100$-solution; the results are always about 0·7% too high. Silver gives good results when similarly titrated at the ordinary temperature, using a silver indicator electrode. As the presence of sulphites interferes with the simultaneous determination of both metals in a solution, the silver is titrated, first using a silver

indicator electrode; the solution is then filtered, a copper electrode inserted, the requisite sodium hydrogen sulphite added, and the copper then titrated as above. By a compensation of errors the results for copper are quite good under these conditions.

A. R. P.

The Electrometric Estimation of Manganese. ERICH MÜLLER and OTTO WAHLE (*Z. anorg. Chem.*, 1923, **129**, 33—40).—Volhard's method of the titration of a manganous salt by means of permanganate $2MnO_4'+3Mn^{\cdot\cdot}+2H_2O=5MnO_2+4H^{\cdot}$ can be carried out electrometrically. The presence of a zinc salt, potassium nitrate, or another electrolyte is shown to be necessary (cf. Sarkar and Dhar, A., 1922, ii, 398). The values obtained are rather low. Near the end-point, an interval of seven minutes is necessary for a constant *E.M.F.* In the presence of hydrogen fluoride, the reaction is as follows: $MnO_4'+4Mn^{\cdot\cdot}+8H^{\cdot}=5Mn^{\cdot\cdot\cdot}+4H_2O$ (cf. Müller and Kopp, A., 1910, ii, 957). In this case, the end-point is sharp, but depends on the composition of the solution. The best results are obtained by using 10 c.c. of 4*N*-sulphuric acid and 8 g. of potassium fluoride per 100 c.c. of the solution. The authors hope to extend the applicability of this method to the analysis of a mixture of ferrous iron and manganese. W. T.

The Separation of Tin from Other Metals. N. HOWELL FURMAN (*Ind. Eng. Chem.*, 1923, **15**, 1071—1073).—An investigation of the precipitation of stannic tin by means of cupferron from such a solution as would be obtained in the McCay method of separating tin and antimony (A., 1909, ii, 351, 1910, ii, 1003) showed that this method of treatment is rapid and accurate. The precipitate on stirring for thirty to forty-five minutes becomes compact and brittle, and is then easy to filter and wash. Manganese, nickel, cobalt, and zinc, if present, remain in the filtrate.

The separation of tin and antimony by precipitation with hydrogen sulphide in dilute hydrofluoric acid solution is incomplete unless the antimony is all in the tervalent state. The method of electolytic precipitation of tin from the solution obtained in the McCay method, as recommended by Kling and Lassieur (A., 1920, ii, 452), has been found to be extremely slow and unsatisfactory. C. I.

Oxidimetric Studies on Antimony. J. KNOP (*Z. anal. Chem.*, 1923, **63**, 81—102).—A large number of titrations of antimony with potassium permanganate under varying conditions have been carried out in order to ascertain those giving the most satisfactory results. Under widely varying conditions of acidity either of hydrochloric or of sulphuric acid or of both, results were obtained which gave only 98·5% of the total antimony if the calculations were based on an atomic weight of 120·2. Every possible source of error was investigated without obtaining any more satisfactory result. Consequently, further series of tests were made by adding an excess of potassium dichromate solution and titrating this excess with ferrous sulphate, using diphenylamine as internal indicator or ferricyanide as external indicator. From the mean of many

very concordant results, again only 98·5% of the antimony present was found and no possible source of error could be discovered. All the results obtained agree with the old atomic weight of 121·9 for antimony, and this seems to confirm the value of 121·8 given in the German atomic weight tables for 1922. A. R. P.

Tables for Sugar Analysis. G. D. ELSDON (*Analyst*, 1923, **48**, 435—443).—Tables are given showing the quantities of dextrose, lævulose, hydrated lactose, anhydrous lactose, maltose, invert-sugar, sucrose, and starch corresponding with weights of cupric oxide (also cuprous oxide and metallic copper) for every mg. from 100 to 460. The tables are based mainly on those published previously by Brown, Morris, and Miller (T., 1897, **100**, 281). W. P. S.

Estimation of Dextrose and Lævulose. F. LUCIUS (*Z. Unters. Nahr. Genussm.*, 1923, **46**, 94—95).—In the estimation of dextrose and lævulose by the method based on the inversion of the latter with dilute inorganic acids (A., 1920, ii, 132), the period of heating may be reduced to three hours by doubling the concentration of acid employed. Any further increase in acid concentration above this figure (20 c.c. of 5*N*-hydrochloric acid and 50 c.c. of sugar solution) leads to an appreciable decomposition of dextrose. A series of ten analyses carried out on mixtures of known composition using this method gave results for dextrose 95—96·7%, and for lævulose 96·1—101% of the amounts actually present. H. C. R.

Biochemical Characterisation of Galactose in a Mixture containing Galactose and Arabinose. MARC BRIDEL and JEAN CHARPENTIER (*Compt. rend.*, 1923, **177**, 908—910).—Emulsin acts on a mixture of galactose and arabinose in 70% alcohol, at 37°, to give β-ethylgalactoside, and galactose may therefore readily be identified, as, for example, in the products of hydrolysis of gum arabic (cf. this vol., i, 540). If the enzyme is renewed from time to time, some ethyl arabinoside is also formed, but, without such renewal, only the galactose is converted into a glucoside. E. E. T.

Estimation of Sugars in Mixtures of Sucrose, Invert-sugar, and Lactose. HANS JESSEN-HANSEN (*Comptes rend. Trav. Lab. Carlsberg*, 1923, **15**, No. 3, 21 pp.).—Sucrose when heated with an alkaline copper solution causes a deposition of cuprous oxide, although this deposition may be reduced to a minimum by a suitable choice of conditions. The quantity of cuprous oxide deposited by a mixture of sucrose and a reducing sugar, or of two reducing sugars, is not equal to the sum of the quantities which each sugar would deposit if it were the only constituent of the mixture. Series of analyses were therefore carried out to determine the amount of copper deposited under standard conditions (1) by pure invert-sugar, (2) by mixtures of sucrose and invert-sugar in which the total weight of sugar present was always equal to 0·240 g.; (3) by pure lactose; (4) by mixtures of 0·200 g. of sucrose with increasing quantities of lactose, and (5) by mixtures of 0·050 g. of lactose with increasing

quantities of invert-sugar. In each case, a formula was calculated to cover the experimental results obtained. The following are the formulæ for the five different cases: (1) $Cu=0{\cdot}20+1{\cdot}97122S-0{\cdot}000735S^2$; (2) $Cu=1{\cdot}94+1{\cdot}97755S-0{\cdot}00079444S^2$; (3) $Cu=0{\cdot}58+1{\cdot}25431L-0{\cdot}000008784L^2$. (4) $Cu=1{\cdot}94+1{\cdot}2597L-0{\cdot}00000025L^2$. (5) $Cu=64{\cdot}91+1{\cdot}897912I-0{\cdot}00050226I^2$. From these formulæ, five sets of tables are calculated giving the number of mg. of the various sugars in question corresponding with quantities of copper of from 0 to 440 mg. The exact procedure used for obtaining the copper is as follows: 8·65 g. of potassium sodium tartrate, 25 c.c. of $3{\cdot}25N$-sodium hydroxide, and 25 c.c. of copper sulphate solution containing 69·278 g. of $CuSO_4,5H_2O$ (=17·592 g. of copper) per litre were mixed just before use in a 150 c.c. conical flask. The sugar solution was added and the total volume made up to 100 c.c. with water. Hydrogen was passed through the flask until all the air was displaced, and the flask then placed in a large boiling water-bath so that the surfaces of the liquid inside and outside the flask were at the same level. The flask was allowed to remain in the bath for exactly five minutes, after which it was removed and the contents were immediately filtered through an Allihn's asbestos tube, using suction. The cuprous oxide was carefully washed with warm boiled water and alcohol and completely transferred to the asbestos tube, which was finally washed with absolute alcohol and ether, dried by suction, and the oxide reduced to metallic copper by passing a current of hydrogen through the tube, heated in an air oven. When completely reduced, the copper was allowed to cool in a current of hydrogen and weighed. In using the tables for the analysis of a mixture of sucrose and invert-sugar, a 2% solution of the sugar is made up, and 50 c.c. of this are inverted according to Nicol. The acid is neutralised and the volume made up to 100 c.c. The invert-sugar in this is obtained from table (1) (=a). The original solution is then analysed, taking a quantity corresponding with 240 mg. of invert-sugar, and from the amount of copper obtained and table (2) the original amount of invert-sugar (=b) is obtained. The original sucrose present is therefore 0·95 (a—b). In the case of mixtures of lactose and sucrose, the approximate quantity of lactose is first obtained from the weight of copper, using table (4). A solution containing about 1% of lactose is then prepared, and 50 c.c. of this are inverted by Nicol's method as above, neutralised, made up to 100 c.c. and the amount of copper obtained from 10 c.c. of this is weighed. The approximate quantity of invert-sugar present in this and consequently of sucrose in the original solution, can then be read off table (5). In order to obtain more exact values, a portion of the original solution containing exactly 200 mg. of sucrose is taken and the quantity of lactose present in this obtained from the weight of copper and table (4). A portion of the inverted solution containing, according to the last analysis, 50 mg. of lactose will then, by using table (5), give the true amount of invert-sugar present, and consequently of sucrose in the original mixture. Concrete examples are given which make the method of using the tables clear. H. C. R.

Estimation of Pentoses and Pentosans. I. Formation and Distillation of Furfuraldehyde. NORVILLE C. PERVIER and ROSS A. GORTNER (*Ind. Eng. Chem.*, 1923, **15**, 1167—1169).—Distillations of materials containing pentoses carried out according to the method of the Association of Official Agricultural Chemists take place from hydrochloric acid of 18—20% concentration instead of from 12% acid, as usually stated. Hydrochloric acid of this concentration has a considerable destructive effect on furfuraldehyde and this is partly responsible for the low yields of furfuraldehyde that are obtained from all pentoses when the official method is used. The passage of a slow current of steam through the distillation mixture is sufficient to carry off the furfuraldehyde as rapidly as it is formed, thereby avoiding its destruction by long contact with strong acid. Details of a method for the distillation of pentoses based on these considerations are given. By means of this method, theoretical yields of furfuraldehyde have been obtained from all the pure pentoses that have been tested. Representative data are given.

H. C. R.

Estimation of Acetyl and on Methylation. KARL FREUDENBERG (*Annalen*, 1923, **433**, 230—237).—[With MAX HARDER.]—Perkin's method (T., 1905, **87**, 107) for the estimation of the acetyl group is improved by the use of aromatic sulphonic acids, particularly of toluenesulphonic acid, instead of sulphuric acid. This procedure offers the following advantages. The hydrolysis requires less time, less charring or formation of by-products occurs, and, in alcoholic solution, the sulphonic acids exert great solvent action. The method is shown to give good results in the analysis of catechin penta-acetate, dextrose penta-acetate, maltose octa-acetate, cellobiose octa-acetate, methylmaltoside hepta-acetate, chloromaltose hepta-acetate, bromoglucose acetate, dichlorocatechin penta-acetate, dimethyl tartrate diacetate, silver acetate, acetanilide, trihydroxypenta-acetatochromic acetate, or dihydroxyhexa-acetatochromic chloride.

[With ERNST COHN.]—Quercetin can be converted into its pentamethyl ether, and phloroglucinol into its trimethyl ether, in yields of, respectively, 75—80% and 80—85% of the theoretical, by conversion into the penta-acetate and triacetate, respectively, and treatment of the latter, in methyl-alcoholic solution, with a large excess of methyl sulphate, followed by the gradual addition of 50% aqueous potassium hydroxide solution (cf. Freudenberg and Purrmann, this vol., i, 697).

W. S. N.

Polarimetric Estimation of Malic Acid. F. AUERBACH and D. KRÜGER (*Z. Unters. Nahr. Genussm.*, 1923, **46**, 97—154).—The method depends on the large increase in the optical activity of malic and tartaric acids caused by uranium and molybdenum compounds. A suitable and constant excess of the compound used to increase the optical activity is employed and the hydrogen-ion concentration of the solution is kept constant at its optimum value by the use of mixtures of buffer salts. The relationship between optical activity and concentration for malic and tartaric

acids was determined experimentally using the above conditions and a process was worked out for estimating these acids when present alone in the form of their sodium salts, with satisfactory accuracy. The molecular rotatory powers of uranium-malic and molybdenum-tartaric acids under the conditions chosen were found to be constant up to a concentration of 0·1 mol. per litre and to be equal to $-700°$ and $+1,044°$, respectively. On increasing the concentration, the values obtained gradually fell. The molecular rotatory power of uranium-tartaric acid increased with the concentration up to a maximum of $+650°$, after which it fell slowly with increasing concentration. The molecular rotatory power of molybdenum-malic acid also increased up to a maximum of $+1,020°$, remaining, however, approximately constant at this figure on further increasing the concentration. The fact that the directions of rotation of uranium-malic and uranium-tartaric acids are opposed, whilst the rotations of the corresponding molybdenum acids are of the same sign enabled a purely polarimetric method of estimating malic and tartaric acids in mixtures to be worked out. Willaman's graphical method of obtaining the percentage of malic acid from the polarimeter readings of the uranium and molybdenum solutions (A., 1918, ii, 249) is adapted to the conditions employed by the authors. The influence of other organic acids on the molecular rotatory powers of these uranium and molybdenum acids was investigated. In the case of uranium-malic and molybdenum-tartaric acids, the alkali salts of other organic acids only slightly decreased the figures obtained. In the case of uranium-tartaric acid, a more considerable disturbance is produced. In the case of molybdenum-malic acid the optical activity is considerably increased by the presence of salts of other hydroxy-acids, citrates almost doubling the molecular rotatory power. In the presence of citric acid, therefore, the polarimetric estimation of malic and tartaric acids in the same solution is impossible and when certain other organic acids are present, the estimation becomes untrustworthy. In determining malic acid polarimetrically in fruit juices and similar acid mixtures, it is therefore advisable not to attempt the simultaneous polarimetric estimation of tartaric acid and to carry out the removal of the sugars, pectins, and colouring matter in such a way that the greater part of the tartaric, citric, and other organic acids are separated from the malic acid at the same time. This can be effected by aid of the different solubilities of the respective barium salts in water and alcohol, by which means the malic acid is obtained as barium malate in aqueous solution containing only small quantities of barium tartrate and barium citrate. The malic acid can be estimated polarimetrically in this solution in the same way as in sodium malate solution. The molecular rotatory power of barium malate in the presence of uranium is somewhat lower than that of sodium malate under similar conditions and increases slowly with the concentration. In the presence of molybdenum, the molecular rotatory power is lower in low concentration and higher in high concentration than is the case with sodium malate. In

order to make the estimation independent of the small quantity of tartrates and citrates present in the barium malate solution, the solution was always saturated with these salts. The relationship between the small quantities of tartrate and citrate present and the polarimeter readings was calculated and that between the concentration of malic acid and the polarimeter readings under these conditions obtained both by experiment and by calculation. By these means malic acid can be estimated with sufficient accuracy from two independent polarimetric measurements even in the presence of tartaric and citric acids. H. C. R.

Analysis of Crude Tartar and Argol. CHEMISCHE FABRIK VORM. GOLDENBURG, GEROMONT & CIE (*Z. anal. Chem.*, 1923, **63**, 111—116).—The solution of the substance in hydrochloric acid is boiled with an excess of potassium carbonate and the filtered liquid is evaporated to a small bulk, treated with potassium chloride, and made exactly neutral to phenophthalein with hydrochloric acid. The liquid is then acidified with diluted acetic acid, digested on the water-bath for a few minutes, and set aside over-night. The precipitate of potassium hydrogen tartrate is collected on a vacuum filter, washed with 20% potassium chloride solution saturated with potassium hydrogen tartrate, and dissolved in 200 c.c. of water. The solution is titrated with sodium hydroxide, using phenolphthalein as indicator.

The above method has been tested in the Chem. Lab. Fresenius (*ibid.*, 116—117) and found to give excellent results. It is cheaper and simpler to carry out than the older method involving precipitation of the potassium hydrogen tartrate by means of alcohol followed by titration as above, but using litmus-paper as indicator. [Cf. *J.S.C.I.*, 1923, Dec.] A. R. P.

The Bromine Number. PAUL BECKER (*Z. angew. Chem.*, 1923, **36**, 539).—A few drops of linseed oil were spread in a thin layer on a sheet of glass (4·5 by 15 cm.) which was then inserted in a horizontal glass tube of 4·6 cm. diameter. A watch-glass containing a few drops of bromine was placed under the glass plate and the tube corked at both ends. After a time, air was passed through the tube, and finally the glass plate was heated in an oven at 50—60° to remove excess of bromine and the increase in weight noted. As an alternative, the glass plate and containing tube may be placed vertically over pieces of glass rod between which a few drops of bromine have been poured. The addition of bromine was complete within half an hour and concordant results were obtained which, when calculated as iodine values, agreed well with those found directly by Wijs's method. W. T. K. B.

New Method of Estimating the Iodine Value of Oils and Fats by using Pyridine Sulphate Dibromide. K. W. ROSENMUND and W. KUHNHEIM (*Z. Unters. Nahr. Genussm.*, 1923, **46**, 154—159).—A solution of pyridine sulphate dibromide in glacial acetic acid can be used for determining the iodine value of oils and fats. The solution is of about the same stability as the Hanus

iodine bromide solution and has the advantages that the results given by it are independent of the amount of excess of the reagent used, that the reaction progresses more rapidly than in the case of the Hanus solution in the case of oils of high iodine values, and that a considerable economy is effected, especially when the excess of reagent is titrated with arsenious acid solution. The reaction is complete in 5 minutes even in the case of linseed oil, and the results obtained agree with those given by Hanus's method within the limits of experimental error. The excess of the reagent can either be treated with potassium iodide and titrated with thiosulphate, or titrated directly with arsenious acid, the two methods giving identical results. Phenol and arsenic may also be estimated by titration with pyridine sulphate dibromide in glacial acetic acid.
H. C. R.

Estimation of the Acetyl Value (of Fats and Oils). Jessie R. Powell (*Ind. Eng. Chem.*, 1923, **15**, 622).—The André-Cook method (A., 1922, ii, 324) is trustworthy, but concordant results cannot be obtained by methods involving the separation of the acetic acid by filtration or distillation. W. P. S.

Detection of Adulterants in Cacao Butter. Marcel Pichard (*Ann. Falsif.*, 1923, **16**, 197—215).—The method proposed depends on the differences observed in the rise of temperature during the solidification of cacao butter and other fats. Fifty g. of the fat are melted at 50°, placed in a vertical tube provided with a thermometer, and surrounded by a jacket through which a current of air at 10° is circulated, and the temperature is noted at definite intervals during the solidification of the fat. The temperature at first falls to a point at which solidification commences, then rises gradually to a maximum, and afterwards falls again. The curve showing the temperature during the solidification of cacao butter is distinctly different from that obtained with other fats. W. P. S.

Benzidine as a Reagent for Aldehydes. P. N. van Eck (*Pharm. Weekblad*, 1923, **60**, 1204—1208).—A large number of aldehydes give good colour reactions in presence of benzidine dissolved in glacial acetic acid. Fatty aldehydes give yellow to orange colorations. Benzaldehyde gives a yellow, crystalline solid, cuminaldehyde an orange solid, anisaldehyde yellow-orange crystals, and phenylacraldehyde dark, blood-red crystals; microchemical tests detect these readily. Vanillin gives a dark, orange-red colour, which becomes red on adding water; the reaction is extremely sensitive.
S. I. L.

Detection and Characterisation of Small Quantities of Vanillin. H. Hérissey and P. Delauney (*J. Pharm. Chim.*, 1923, [vii], **28**, 257—262).—When aqueous solutions of vanillin are oxidised with ferric chloride, a blue coloration is formed, which, when the mixture is heated for five minutes in the boiling water-bath and then cooled, disappears and is replaced by a precipitate (thin, microscopic, colourless needles, m. p. 302—305°) of dehydrodi-

vanillin, $[C_6H_3(CHO)(OMe)\cdot OH]_2$. This precipitate may be ...ed, and collected by centrifuging, in solutions containing as ... as 0·01% of vanillin. Vanillin is somewhat difficultly volatile in steam, but may be detected and characterised in plant extracts containing as little as 0·05%, as follows. Twenty c.c. of the solution to be tested are heated in a bath containing a solution of calcium chloride at 130—140°, and two fractions of 10 c.c. of distillate are collected. Further quantities of 10 c.c. of water are added to the residue and again distilled off, this being repeated until nine or ten such fractions have been collected. The presence of vanillin in these fractions is then determined as above with ferric chloride.

W. T. K. B.

The Salt Error of Nitramine (Picrylmethyl Nitroamine). I. M. KOLTHOFF (*Rec. trav. chim.*, 1923, **42**, 964—968; cf. A., 1922, ii, 222).—Using nitramine as an indicator, the salt error of electrolytes with univalent ions is $-0{\cdot}09$ (in p_{OH}) in seminormal solution. In normal solution, the error depends on the salt, and is greater for potassium than for sodium salts. The error increases with rising valency of the anion. Thus the correction for N-KCl is $+0{\cdot}16$, for N-K_2SO_4, $+0{\cdot}30$, and for N-$K_4Fe(CN)_6$ it is $+0{\cdot}34$ in p_{OH}. H. H.

Review of Methods for the Estimation of Acetanilide. EDWARD S. ROSE (*Amer. J. Pharm.*, 1923, **95**, 743—754).—Both Seidell's tribromoaniline method (A., 1907, ii, 914) and the acetyl radicle method, in which the acetic acid liberated by hydrolysis with dilute sulphuric acid and distilled off is titrated, give good results in estimating acetanilide. When interfering substances have to be removed, the former method is somewhat more rapid. One method may be made a check on the other by distilling off and titrating the acetic acid and titrating the acid residue containing the aniline with bromide–bromate solution as in the tribromoaniline method. With preparations containing such substances as solid and powdered extracts, alkaloids and their salts, antipyrine, or pyramidone, the acetyl radicle method is more advantageous as it can be applied directly to the residue from the chloroform extraction. When phenacetine is present, it should be removed as periodide (Emery, *A.*, 1914, ii, 755). H. C. R.

The Triketohydrindene Reaction. V. S. SADIKOV and N. D. ZELINSKI (*Biochem. Z.*, 1923, **141**, 105—108).—In contradistinction to the coloration formed by ninhydrin and hydroxy-compounds, that produced in the presence of amino-acids is resistant to boiling, to decinormal alkali, and to 1% phosphoric acid, and is soluble in amyl alcohol. Methylalanine gives the reaction after prolonged boiling. The ninhydrin pigment is unstable and slowly disappears, even when air is excluded. The esters of monocarboxylic amino-acids and dicarboxylic imino-acids give a carmine-red pigment insoluble in amyl alcohol, and after hydrolysis with acid an amyl alcohol soluble blue pigment. Free methylaspartic acid gives the reaction, but its ester does not. 3-Amino-1-methyl*cyclo*pentanecarboxylic acid gives a violet colour extractable by amyl alcohol.

It is concluded that a number of typ
acids and the ninhydrin reagent are

Estimation of Hydrogen Cyani
E. KOHN-ABREST and J. RICARDO
771—773).—The powdered plant m THORS' NAMES.
37° for four hours, or at the ordinar
Purified air is then blown through
through standard potassium hydroxide
cyanide absorbed by the latter being estimated ACTS.
The results of analyses of various specimens of Pha...
(eleven varieties) show the method to be as satisfactory
ordinary (distillation) method. E. E. T.

Qualitative Scheme for the Detection of Cyanamide and Related Compounds. G. H. BUCHANAN (*Ind. Eng. Chem.*, 1923, **15**, 637—640).—Systematic directions are given for the detection of ammonia, cyanamide, cyanide, dicyanodiamide, guanidine, guanyl carbamide, nitrate, thiocyanate, thiocarbamide, and carbamide in fertiliser mixtures containing any or all of these compounds.

W. P. S.

An Iodometric Method for Estimating Uric Acid in Urine. OTTO FÜRTH, JOSEPHA URBACH, and PAUL WERMER (*Biochem. Z.*, 1923, **141**, 236—247).—The authors have devised a rapid method for estimating uric acid in urine which does not necessitate lengthy and troublesome filtrations and washings. Five c.c. of urine, measured into a 50 c.c. centrifuge tube, are made alkaline by the addition of sodium carbonate and 5 c.c. of 30% ammonium chloride are added. The tube is left for two hours, centrifuged for five minutes, and after separation of the supernatant liquid, the precipitated ammonium urate is stirred with 5 c.c. of 10% ammonium sulphate and again centrifuged for six or seven minutes. The washed precipitate is dissolved in 50 c.c. of 0·1*N*-sodium hydroxide, 20 c.c. of 0·01*N*-iodine solution are added, the solution is at once acidified by the addition of 70 c.c. of 0·1*N*-sulphuric acid, and the excess of free iodine is titrated with 0·01*N*-sodium thiosulphate. Under the conditions employed, 1 mol. of uric acid takes up 3·5 atoms of iodine. The estimation is completed in two and a half hours, including the two hours allowed for separation of the ammonium urate.

J. P.

The Relationship between Colour and Constitution in Azo-dyes. MIECZYSŁAW DOMINIKIEWICZ (*Roczniki Chemji*, 1923, **2**, 314—335).—A theoretical paper in which the known facts relating to azo-dyes are reviewed and discussed mainly from the point of view of the quinonoid theory. For the "colour analysis" of various dyes, a method is suggested whereby any given colour is matched by mixing three fundamental colours (blue, red, and yellow) and the quantities of each are noted. The dyes chosen as standard are patent blue V, rhodamine B, and quinoline yellow O; the standard aqueous solutions of these should contain 0·6350, 0·4785, and 0·8658 g. per litre, respectively. G. A. R. K.

vanillin, [C_6H_3(CHO)(OMe)·d for Estimating ... ed, and collected by ce. H. KLEINMANN (Biochem. ... as 0·01% of vanillin. V nephelometric estimation of in steam, but may be detected are added, in the order ... containing as little as 0·05%, as of a 20% solution of sodium to be tested are heated in a bat uted to 20 c.c. The result chloride at 130—140°, and two nst suitable standards in collected. Further quantities of nephelometer, reaches a m residue and again distil permanent for at least an hour. It such fractions b rtional to the amount of protein present. these fracti the acidity of the solution, or the addition of am phate, magnesium sulphate, or thymol, is without infl the results, nor does the presence of the soluble products hydrolysis interfere with the determination. The method used for the estimation of quantities of protein as small as

The Estimation of Fibrinogen. WILHELM STA (*Biochem. Z.*, 1923, **140**, 203—229).—A lengthy critical s the various gravimetric, Kjeldahl, and refractometric hitherto employed in estimating fibrinogen, which is based on refractometric measurements on native hirudin, oxalate, and fluoride plasmas and sera. In place of t calcification" method of Leendertz, the author has emp new process dependent on refractometric determinations on plasma, and on the serum after separation of the preci fibrinogen produced by heating for five minutes to 5 determination can be carried out on 0·5 c.c. of plasma.

Estimation of Fibrinogen by Precipitation with Sulphate compared with the Precipitation of Fibrin Addition of Calcium Chloride. PAUL E. HOWE (*J. Bio* 1923, **57**, 235—240).—Results in good agreement with the by Cullen and Van Slyke's method (A., 1920, ii, 398) ha obtained for the fibrinogen content of blood by estima nitrogen content before and after precipitation with 10·6% sulphate (or certain other salts) at 37°. Similar resu obtained by Gram's (A., 1922, ii, 240), Foster and Whipple *J. Physiol.*, 1921—1922, **58**, 393), and Wu's (A., 1922, methods.

The Estimation of Fibrinogen in Blood Plasma. RUSZNYÁK and I. BARÁT (*Biochem. Z.*, 1923, **141**, 476— nephelometric method for the estimation of fibrinogen in bloo is described. 0·1 C.c. of citrate plasma is treated with 50 acid solution of ammonium sulphate (1 part of 0·2*N*-hyd acid, 1 part of saturated ammonium sulphate), and the opalescence, which is due to the total plasma proteins, is c with that produced by fibrinogen alone when 0·4 c.c. of th is treated with 25 c.c. of a 27% saturated ammonium solution.

INDEX OF AUTHORS' NAMES.

TRANSACTIONS AND ABSTRACTS.

1923.

(Marked T., and A., i and A., ii respectively.)

C.

D.

E.

F.

H.

I.

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K.

M.

P.

R.

T.

U.

V.

W.

INDEX OF SUBJECTS.

TRANSACTIONS AND ABSTRACTS.

1923.

(Marked T., and A., i and A., ii respectively.)

A.

H.

J.

M.

R.

T.

(o-*Xylene*, *Me* : *Me* = 1:2 ; m-*xylene*, *Me* : *Me* = 1:3 ; p-*xylene*, *Me* : *Me* = 1:4.)

X

(o-*Xylene*, *Me* : *Me* = 1:2 ; m-*xylene*, *Me* : *Me* = 1:3 ; p-*xylene*, *Me* : *Me* = 1:4.)

INDEX TO PATENTS.

ERRATA.

Vol. 82 (Abstr., 1902).

Page Line
i. 31 13* *for* "favour" *read* "retard."

Vol. 98 (Abstr., 1910).

i. 532 6* *for* "When X" *read* "When R."
3* ,, "magnesium derivative of bromoquinol dimethyl ether" *read* "bromomagnesium derivative of quinol dimethyl ether."

Vol. 124 (Abstr., 1923).

i. 171 8* *for* "Blanch" *read* "Blanck."
i. 449 24* ,, "Calvary" *read* "Calvery."
i. 613 19 ,, "Mogco" *read* "Mogoi."
i. 660 28 ,, "$\beta\gamma$-diaminopropionic acid" *read* "$\alpha\beta$-diaminopropionic acid."
i. 756 6 ,, "Hentikka" *read* "Hintikka."
i. 1124 22 and 23 for "5-*chloro*-1:3-*dihydroxynicotinonitrile*" read "6-*chloro*-2:4-*dihydroxynicotinonitrile*."
20* ,, "1:3:5-" *read* "2:4:6-" (in each case).
18* ,, "5-*chloro*-1:3-*dihydroxynicotinamide*" read "6-*chloro*-2:4-*dihydroxynicotinamide*."
8* ,, "5-*chloro*-1:3-*dimethoxynicotinonitrile*" read "6-*chloro*-2:4-*dimethoxynicotinonitrile*."
3* ,, "1:3:5-" *read* "2:4:6-"
ii. 11 16* *for* "Politzer" *read* "Pollitzer."
ii. 32 21, 22 ,, "face centered cube" *read* "hexagonal close packed."
ii. 186 11* ,, "acetic" *read* "tartaric."
ii. 214 15* ,, "freed" *read* "free."
14* *delete* "by passing it through a tube immersed in liquid air."
ii. 440 2* ,, "Thalhimer" *read* "Thallinner."
ii. 448 12 ,, "Nanusso" *read* "Nanussi."
ii. 535 10 ,, "Viehaever" *read* "Viehoever."
ii. 717 1 ,, "unable" *read* "able."

Collective Index 1913—1922 (Authors).

Page
209 col. i. last two entries should be under "**Dale**, *Henry Hallett*, and *Harold Ward* **Dudley**" in col. ii.

* From bottom.